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THE APPLICATION OF THIOSALTS IN ANALYSIS
IV. A NEW SCHEME OF QUALITATIVE ANALYSIS

Part B. INSOLUBLE SUBSTANCES IN QUALITATIVE ANALYSIS

by

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In a previous paper[1] a new scheme was put forward for the qualitative analysis of mixtures containing common elements, based on the formation and subsequent decomposition of the thiosalts. It was also shown that certain compounds are likely to be left as an "insoluble" residue after the mixture is subjected to standard acid treatment as outlined in *Procedure I* of this paper.

In a publication[2] from the University of Allahabad, a new scheme was proposed for the analysis of "insoluble substances" containing the compounds of the common as well as rare elements, with a brief review of the relevant properties of these compounds.

In this paper the author intends to give a mere outline of the procedure to be followed in case an insoluble residue is obtained after subjecting the mixture (containing only common elements) to standard acid treatment.

The insoluble residue may contain

Sulphates: $BaSO_4$, $SrSO_4$, $Cr_2(SO_4)_3$ (anhydrous), $PbSO_4$

Halides: AgCl, $CrCl_3$ (violet), CaF_2 (fluorspar)

Ignited Oxides: Al_2O_3, Cr_2O_3, SnO_2, Sb_2O_4, SiO_2

Complex ferro- and ferricyanides: Prussian Blue, Turnbull's blue, and cupric ferro- and ferricyanides

Stannic phosphate.

The following steps may be taken to identify systematically the compounds present in the insoluble residue:

Procedure I

Extract the residue with saturated ammonium acetate, $PbSO_4$ dissolves completely. Test the filtrate for lead with potassium chromate. A yellow precipitate shows the presence of lead sulphate.

Procedure II

Boil the insoluble residue from *Procedure I* with 4*N* sodium hydroxide solution and filter. Concentrate the filtrate to a small volume, evaporate to dryness with *aqua regia* to dehydrate silica and decompose the ferro- and ferricyanides. Take up the residue with 2*N* hydrochloric acid, filter and analyse as follows:

Ppt. 2 SiO_2,H_2O.	Filt. Chlorides of Al, Cr, Fe and Sb. Treat with 1N Na_2S in excess and filter.	
Test for silica by SiF_4 test in a lead or platinum dish.	Ppt. $Al(OH)_3$, $Cr(OH)_3$, Fe_2S_3. Test as usual.	Filt. Thiosalt of Sb. Acidify with dil. HCl. Boil and filter. An orange ppt. Shows **Sb**

The precipitate obtained after boiling with 4N sodium hydroxide solution is extracted with dilute hydrochloric acid and the solution containing the chlorides of Fe, Cr and Cu analysed as follows:

Add 1N Na_2S in excess and filter. Treat the precipitate of hydroxides and sulphides with dilute hydrochloric acid and filter.

Ppt. CuS (black). Test as usual.	Filt. Chlorides of Fe and Cr. Test as usual.

Procedure III

Treat the residue left after extraction with dilute hydrochloric acid in *Procedure II* with dilute ammonium hydroxide and test the filtrate for silver. If silver is found in the ammoniacal solution, test for the following acids which may have been decomposed by *aqua regia* with the formation of AgCl.

(a) Treat a portion of the original mixture with zinc and dilute sulphuric acid and test for chloride, bromide, iodide, cyanide and thiocyanate as usual.

(b) Test for ferro- and ferricyanides in the sodium carbonate extract of the original mixture for the detection of the acid radicals even in case silver is absent, as these acids are likely to be present due to other insoluble complex ferro- and ferricyanides.

Procedure IV

Fuse the residue with NaOH, Na_2CO_3 and KNO_3 (if coloured) in sufficiently large excess. The changes which will be brought about may be represented conveniently as follows:

$BaSO_4$	$SrSO_4$	CaF_2	$Cr_2(SO_4)_3$	Cr_2O_3	SnO_2	Sb_2O_4
$\downarrow$	$\downarrow$	$\downarrow$	$\downarrow$	$\downarrow$	$\downarrow$	$\downarrow$
$BaCO_3$	$SrCO_3$	$CaCO_3$				
+	+	+				
Na_2SO_4	Na_2SO_4	NaF	Na_2CrO_4	Na_2CrO_4	Na_2SnO_3	Na_3SbO_4
			+			
$NaAlO_2$	Na_2SiO_3		Na_2SO_4	$(Na_2SnO_3 + Na_3PO_4$		
$\uparrow$	$\uparrow$			$\uparrow$		
Al_2O_3	SiO_2			$Sn_3(PO_4)_4$		

(a) Crush and boil the fused mass with water. All the sodium compounds between the two lines will pass into solution. Filter and test the filtrate for
(i) Sulphate, phosphate, fluoride and silicate
(ii) Al, Cr, Sb and Sn.

(b) Boil the residue not dissolved by water in dilute acetic acid, filter and test the filtrate for Ba, Sr and Ca as usual.

Procedure V

SnS_2 (mosaic gold) and HgS (black) will undoubtedly go completely into solution on treatment with standard acids in *Procedure I*, but test for the sulphide radical in the residue left after boiling the original mixture with a saturated solution of sodium carbonate, with zinc and hydrochloric acid. These will be decomposed to give hydrogen sulphide.

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SUMMARY

A scheme has been proposed for the systematic detection of compounds in the insoluble residue btained in qualitative analysis of the common elements.

RÉSUMÉ

L'auteur propose un schéma de détection systématique des composés pouvant se trouver dans s résidus insolubles, obtenus lors de l'analyse qualitative des éléments courants.

ZUSAMMENFASSUNG

Der Autor schlägt ein Schema vor zur systematischen Auffindung der Verbindungen, welche ch in unlöslichen Rückständen befinden können, die man während der qualitativen Analyse er gebräuchlichen Elemente erhalten hat.

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IDENTIFICATION SPÉCIFIQUE DES ACIDES AMINÉS ET DES VITAMINES PAR L'INDICE DE RÉFRACTION ET LA TEMPÉRATURE EUTECTIQUE

APPLICATION A LA CHROMATOGRAPHIE SUR PAPIER ET AU CONTRÔLE

par

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Les deux classes de composés envisagés ici ne bénéficient pas des moyens d'identification courants (température de fusion, des individus ou de leurs dérivés) des corps organiques[1]. D'autre part, leur identification par la solubilité, le pouvoir rotatoire, la densité, présente soit des lacunes, soit un manque de conditions standard. Le R_F en chromatographie est actuellement le moyen d'identification le plus sûr, mais demande à être contrôlé[2]. L'identification de ces substances doit d'autre part tenir compte de leur fragilité aux réactifs et à la chaleur, aussi dans certains cas, de leur prix élevé. C'est pourquoi, nous avons envisagé pour cette contribution un moyen réalisable sur aussi peu de substance que possible (quelques microgrammes) par des techniques susceptibles de ne pas démolir les individus.

L'indice de réfraction semble à ce point de vue préférable: quelques microgrammes suffisent à sa détermination par immersion à la température ordinaire et la précision à laquelle on peut prétendre est de 0.002 unités, si l'on travaille en lumière monochromatique et à température constante. Cette constante a l'avantage de pouvoir se mesurer sur un cristal faisant partie d'un mélange. Par conséquent, elle est susceptible d'être utile pour l'analyse de taches chromatographiques (après élution et évaporation du solvant ou après sublimation). L'observation des lignes de Becke dans des liquides de référence (dont l'indice est connu à la 4ème décimale près), sous le microscope polarisant, a été décrite ainsi que la manière de procéder pour déterminer les indices conventionnels n_p et n_g des individus, sans procéder à des coupes orientées[3].

Nous donnons les renseignements à ce sujet concernant 38 acides aminés et 14 vitamines. Ces renseignements peuvent, sans aucun doute, servir dans le contrôle proposé et surtout dans le contrôle de pureté des individus. Mais il apparaît que la spécificité de cette constante n'existe que pour 50% des cas d'acides aminés examinés et que dès lors il est impossible de s'en tenir uniquement à cette détermination pour identification. Il a été prouvé que l'origine des acides aminés et des vitamines ne joue aucun rôle dans la valeur de l'indice[3].

D'autre part, d'intéressants effets de structure sur la grandeur de l'indice sont perceptibles et ont été notés au cours de ce travail.

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* Dir.: A. LACOURT.

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Ont une action:

— la position des fonctions NH_2 et COOH (β- et α-alanine et acide ε-aminocaproïque)

— l'allongement de la chaîne (DL-α-alanine, L-α-alanine, acide DL-α-aminobutyrique, DL-norvaline, DL-norleucine, L-norleucine)

— la ramification de chaîne (*iso*propylique: DL-norvaline, DL-valine, L-valine, DL-norleucine, DL-leucine, L-leucine; *iso*butylique: DL-norvaline, DL-leucine, DL-*iso*leucine)

— la substitution d'un CH_3 par COOH, C_6H_5, C_6H_4OH, CH_2OH, CH_2SH et le remplacement d'un CH_2OH par un CH_2SH.

TABLEAU I

INDICES DE RÉFRACTION DES ACIDES AMINÉS (MÉTHODE PAR IMMERSION, ±0.002)*

Acides expérimentés	n_p *à 20°*	n_g *à 20°*	*Poids moléculaire*	*Densité*
Glycine	1.619	1.657	75.07	1.601 1.607
β-Alanine	1.524	1.583	89.09	1.404
Ac. ε-Aminocaproïque	1.504	1.536	131.17	—
DL-α-Alanine	1.539	1.579	89.09	1.424
L α-Alanine	1.517	1.560	89.09	1.401
Ac. DL-α-Aminobutyrique	1.517	1.543	103.12	1.231
DL-Valine	1.580	1.602	117.15	1.316
L-Valine	1.553	1.585	117.15	1.230
DL-Norvaline	1.481	1.502	117.15	—
DL-Leucine	1.538	1.558	131.17	1.191
L-Leucine	1.525	1.543	131.17	1.165
DL-*Iso*leucine	1.552	1.581	131.17	—
L-*Iso*leucine	1.536	1.560	131.17	—
DL-Norleucine	1.522	1.558	131.17	1.169
L-Norleucine	1.524	1.554	131.17	—
Ac. DL-Aspartique	1.524	1.628	133.10	1.663
Ac. L-Aspartique	1.504	1.620	133.10	—
Ac. DL-Glutamique	1.526	1.539	147.13	1.460
Ac. L-Glutamique	1.504	1.619	147.13	1.538
DL-β-Phénylalanine	1.619	1.657	165.19	—
L-β-Phénylalanine	1.607	1.660	165.19	—
DL-Tyrosine	1.560	1.658	181.18	—
L-Tyrosine	1.525	1.640	181.18	1.456
L-Arginine.HCl	1.572	1.595	174.21+HCl	—
L-Histidine.HCl	1.593	1.620	155.16+HCl	—
L-Histidine	1.525	1.619	155.16	—
DL-Lysine.2HCl	1.545	1.568	146.19+2HCl	—
L-Lysine.2HCl	1.560	1.569	146.19+2HCl	—
DL-Tryptophane	1.607	1.658	204.22	—
DL-Thréonine	1.525	1.597	119.10	—
L-Thréonine	1.526	1.593	119.10	—
DL-Méthionine	1.568	1.604	149.21	1.340
L-Méthionine	1.560	1.584	149.21	—
DL-Sérine	1.558	1.578	105.90	1.537
L-Cystéine	1.608	1.622	121.15	—
L-Proline	1.552	1.576	115.13	—
Créatine	1.528	1.586	131.14	—
Créatinine	1.620	1.742	113.12	—

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* La température d'observation a été 20° ± 0.1° dans l'éclairage au sodium.

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Dans tous les cas des acides aminés, le passage d'un isomère DL à un isomère L est marqué par une diminution de la valeur du plus petit des indices, n_p (voir Tableau 1).

Tous les acides aminés sont solubles dans l'eau et l'évaporation de leur solution à la température ordinaire améliore souvent l'aspect des cristaux destinés aux déterminations d'indices. Il ne faut pas qu'ils soient trop épais. Dans ce cas, mieux vaut les recristalliser que les broyer. La sublimation permet aussi d'obtenir des cristaux convenables; tous les acides examinés — sauf le DL-aspartique et l'arginine — subliment à température plus basse que la fusion[4].

Avec les vitamines (voir Tableau II), nous n'avons jamais procédé autrement que par cristallisation préalable à la détermination des indices. Au départ, tous les acides aminés ont été examinés au point de vue de leur pureté (constance de l'indice, stabilité d'eutectique après cristallisation).

TABLEAU II

INDICES DE RÉFRACTION DES VITAMINES (MÉTHODE PAR IMMERSION, ± 0.002)*

Vitamines	*T°Fus.*	n_p *à 20°*	n_g *à 20°*	*Indice à la fusion (méthodes des poudres)*[5]
Nicotinamide	129/131	1.477	1.742	1.5502 à 130° 1.5403 à 156°
Ac. Nicotinique	234/237	1.481	1.742	1.4936 de 240° à 241°
Ac. *Iso*nicotinique	137	1.445	1.742	
Ac. *o*-Aminobenzoïque	145	1.504	1.746	1.5700 de 145° à 147° 1.5611 de 165° à 168°
Ac. *m*-Aminobenzoïque	174/179	1.530	1.742	1.5611 de 175° à 178°
Ac. *p*-Aminobenzoïque	187	1.530	1.742	1.5795 à 193°
Pyridoxine . 2HCl	160 déc.	1.553	1.697	
Pyridoxal . 1HCl	207/214	1.560	1.623	1.5897 à 207°
Adermine (Vit.B6)				1.6011 „
Aneurine (Vit. B_1)	245/250	1.598	1.700	
Hespéridine (Vit. P)	251/254	1.553	1.685	
Vitamine B_2	282 déc.	1.658	1.658	
Ac. Folique	infus. 250 déc.	1.560	1.742	
Ac. L-Ascorbique	190/192	1.481	1.694	1.5101 à 195° 1.5204 „
Ac. D-*Iso*ascorbique		1.536	1.688	

* Observations à 20° ± 0.1° en éclairage au sodium.

L'étude systématique *des eutectiques binaires* a révélé pour les acides aminés des résultats beaucoup plus spécifiques, permettant le plus souvent de distinguer les isomères les uns des autres.

La technique employée pour la préparation des mélanges ne peut faire usage de la méthode de contact, à cause de la fragilité des substances étudiées. On procède par simple broyage des individus entre deux porte-objets ou par mise en solution. Il s'agit de voir la première fusion dans ce mélange chauffé sous le microscope polarisant[3]. 18 acides et 9 vitamines ont été examinés ainsi.

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Les effets de structure se sont encore révélés beaucoup plus déterminants des eutectiques que la proximité des points de fusion des partenaires ou que leur système cristallin.

Bon nombre d'eutectiques liquides à la température ordinaire n'ont pas encore été étudiés, mais mériteraient de l'être. Ils sont néanmoins caractéristiques déjà. Un bon nombre de ces eutectiques sont fusibles en-dessous de 100° et ne risquent donc pas d'altérer les acides aminés chauffés. L'identification par les eutectiques seuls n'est pas possible. Elle l'est davantage si on la combine avec la détermination de l'indice de réfraction. Les acides aminés forment des eutectiques entre eux et aussi avec un grand nombre de partenaires. Les tableaux qui suivent montrent l'usage que l'on peut faire de ces deux propriétés pour aboutir à l'identification des individus et préciser auquel des isomères on a affaire. Le choix des eutectiques est très grand pour ne pas être gêné dans ses conclusions, même dans les cas les moins favorables.

Le groupe important des *leucine, isoleucine* et *norleucine*, par exemple, qui migrent souvent en une seule tache[5] sont reconnaissables par des indices différents dans le mélange sublimé du papier.

D'autre part, les individus isolés ont des températures de fusion eutectique nettement différentes avec plusieurs partenaires. Pour des acides comme la *glycine* et la *β-phénylalanine* difficiles à reconnaître par leurs températures de fusion et par leurs indices de réfraction, la température de fusion eutectique de mélanges binaires permet de décider auquel des deux l'on a affaire (voir Tableaux III, IV A et IV C).

TABLEAU III

GLYCINE ET DL-β-PHENYL ALANINE

	Glycine *T°Fus. 240/247*	DL-*β-Phénylalanine* *T°Fus. 225/240 déc.*
Indices de réfraction		
n_p à 20°	1.619	1.619
n_g à 20°	1.657	1.657
Partenaire	*Fusion des eutectiques binaires*	
Ac. Malonique	liquide	105
Ac. Succinique	144	158/159
Ac. Tartrique	liquide	130
Ac. Ascorbique	130/131	159/160
Ac. Hippurique	175/176	160

Pour le groupe des *acides aspartiques* et *glutamiques* dont la séparation chromatographique est assez rare, on est aidé dans l'analyse de telles taches globales par le fait que l'acide aspartique ne sublime pas tandis que les glutamiques subliment. Le tableau des identifications spécifiques montre le parti que l'on peut tirer des deux propriétés qui ont été étudiées ici, en vue de l'identification des acides aspartiques, DL-et L-glutamiques (voir Tableau IV B).

TABLEAU IV

IDENTIFICATION SPÉCIFIQUE DES ACIDES AMINÉS

A. GLYCINE, ACIDE ε-AMINOCAPROIQUE, DL-α-, L-α- ET β-ALANINE

Propriétés physiques	*Glycine*	*β-Alanine*	*ε-Amino caproïque*	*DL-α-Alanine*	*L-α-Alanine*
Température de fusion	240/247	202/205	205/210	257 déc.	266 déc.
Densité	1.601 1.607	1.404		1.424	1.401
Indice de réfraction (20°, Na)					
n_p	1.619	1.524	1.504	1.539	1.517
n_g	1.657	1.583	1.536	1.579	1.560

Partenaire	*T° Fus. parten.*	*Température de fusion des eutectiques binaires*				
Glycine	240/247		166/168	193/195	négat.	négat.
β-Alanine	202/205	166/168	—	169	négat.	négat.
ε-Aminocaproïque	205/210	193/195	169	—	192/194	180/182
DL-α-Alanine	257 déc.	négat.	négat.	192/194	—	négat.
L-α-Alanine	266 déc.	négat.	négat.	180/182	négat.	—
DL-α-Aminobutyrique	200	négat.	négat.	174/177	négat.	négat.
DL-Aspartique	> 310	202/203	155/156	145/148	217	214
DL-Glutamique	180/183	172/174	158/160	144/146	165	165/166
L-Glutamique	194/198	185/187	163/164	154/156	189	176/177
Ac.Oxalique (subl.)	189	131/132	108	102	146/147	163
Ac.Malonique	131/136	liq.	liq.	liq.	liq.	liq.
Ac.Succinique	188	144/145		97	151/152	150/152
Ac.Adipique	154	146	90/92	69	146/147	140/142
Ac.Tartrique	169	liq.	liq.	78/78.5	liq.	liq.
Ac.Ascorbique	186	130/131	101/104	92	139/141	141
Glucose	146	140 déc.	141 déc.	115 déc.	137/139	135/136
Lactose	201	déc.	déc.	133/134	164/166	162/164
Mannitol	167	156		147/148	159	161/162
Ac.*o*-Hydroxybenzoïque	157	négat.	liq.	liq.	148/149	138
Ac.*p*-Hydroxybenzoïque	214	négat.	115/117	131	172/173	181/182
Nipagine M	127.5	119/120	123	112/113	118/119	124/126
Aspirine	133/144	126/127	95/97	69/71	123	124
Hydroquinone	172	négat.	112/114	140	163/165	161/162
Résorcine	110.5	104/106	liq.		103	96
Pyrogallol	133	105/106	,,	71/74	102	109/110
Ac. Hippurique	190	174/176	118/120	128	153/154	164/166
α-Chloracétamide	119.5	115/116	83/86	96/100	113	117/118
Saccharine	228	170/171	liq.	liq.	166/167	165/166
Urée (subl.)	135	125/126	112	115/116	126	124
Dicyandiamide	210	179/180	151/153	154/155	175/176	175/177
Thiourée	178/179	163/164	132/135	134/135	164/166	159/163

B. ACIDES DL-ASPARTIQUE ET DL- ET L-GLUTAMIQUES

Propriétés physiques	*Ac.DL-Asparique*	*Ac.DL-Glutamique*	*Ac.L-Glutamique*
Température de fusion	> 310	180/183	194/198
Densité	1.663	1.460	1.538
Indice de réfraction (20°, Na) n_p	1.524	1.526	1.504
Indice de réfraction (20°, Na) n_g	1.628	1.539	1.619

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TABLEAU IVB (SUITE)

Partenaire	*T° Fus. parten.*	*Température de fusion des eutectiques binaires* *Ac. DL-Aspartique*	 *Ac. DL-Glutamique*	 *Ac. L-Glutamique*
Glycine	240/247	202/203	172/174	185/187
β-Alanine	202/205	155/156	168/160	163/164
ε-Aminocaproïque	205/210	145/148	144/146	153/156
DL-α-Alanine	257 déc.	217	165	189
L-α-Alanine	266 déc.	214	165/166	176/177
DL-α-Aminobutyrique	200	179/182	159/162	176/178
DL-Norvaline	275 déc.	235/237	174/176	186
DL-Norleucine	250 déc.	242/243	173/175	187/188
DL-Aspartique	> 310		172/173	187/189
DL-Glutamique	180/183	172/173		173
L-Glutamique	194/198	187/189	173	
L-Arginine. HCl	208/220			188/191
L-Histidine. HCl	250 déc.			191/192
DL-Tryptophane	250 déc.			191
L-Tryptophane	250 déc.			négat.
DL-Thréonine	233/235			185/187
DL-Méthionine	235 déc.			188/190
L-Cystéine	225 déc.			189/192
L-Cystine	220 déc.			187/190
L-Proline	222			159/164
Créatine	250/252			180/184
Créatinine	240 déc.			184/186
Ac. Oxalique (subl.)	189	45/46	50/52	64/65
Ac. Malonique	131/136	99/102	60/63	101
Ac. Succinique	188	177/180	156/158	170/171
Ac. Tartrique	169	141/143	95/98	135
Ac. Ascorbique	186	170/171	148/150	165/166
Ac. p.-Hydroxybenzoïque	214	négat.	172/173	182/184
Aspirine	135	négat.	125 subl.	122
Ac. Hippurique	190	négat.	165/166	174/175
Saccharine	228	218/219	174/175	185/187
Dicyandiamide	210	168/170	150/152	166/167
Thiourée	178/179	négat.	156/158	169/170

C. DL-β PHÉNYLALANINE, DL-LEUCINE, DL-ISOLEUCINE ET NORLEUCINE

Propriétés physiques		DL-β- *Phénylalanine*	DL- *Leucine*	DL- *Isoleucine*	DL- *Norleucine*
Température de fusion		225/240	242/252	235	250 déc.
Densité			1.191		1.170
Indice de réfraction (20°, Na) n_p		1.619	1.538	1.552	1.522
Indice de réfraction (20°, Na) n_g		1.657	1.558	1.581	1.558
Partenaire	*T° Fus. parten.*	*Température de fusion des eutectiques binaires*			
Ac. Oxalique (subl.)	189	129	150/151		127
Ac. Malonique	131/136		liq.	68/70	83
Ac. Adipique	154		139/142	143	146/147
Ac. o-Hydroxybenzoïque	154/157	138/140	145/146	140	141/144
Ac. p-Hydroxybenzoïque	214	197	205	négat.	189
Ac. Hippurique	190	160	173/174	168/169	170
Ac. Diiodohippurique	209/218		203/204	190	197/200
α-Chloracétamide	119.5		109/110	± 100	négat.
Saccharine	228	172/176	187/188	171/172	186
Dicyandiamide	210		192	189/190	183/188
2.4.D.N.Phénylhydrazine	195/202		185/187	184	175/179
ε-Aminocaproïque	205/210	186	201/203	193/195	188
Ac. DL-Aspartique	> 310	négat.	négat.	négat.	242/243
Ac. DL-Glutamique	180/183	négat.	négat.	négat.	173/175
Ac. L-Glutamique	194/198	négat.	négat.	négat.	187/188

TABLEAU V

EUTECTIQUES BINAIRES DES VITAMINES

Vitamines	*T° Fus. vitamines*	*Partenaires*	*T° Fus. partenaires*	*T° Fus. eutectiques (loc.cit. 5)*
Nicotinamide	129/131	Acétanilide	115	89
		Phénacétine	135	106
Ac.Nicotinique	234/237	Salophène	190	180
		Dicyandiamide	210/212	150
Ac.*o*-Aminobenzoïque	145	Phénacétine	135	98
		Benzanilide	163	122
Ac.*m*-Aminobenzoïque	174/179	Benzanilide	163	141
		Salophène	190	152
Ac.*p*-Aminobenzoïque	187/(193)	Benzanilide	163	140
		Salophène	190	183
Adermine (vit. B_6)	207/214	Salophène	190	183
		Dicyandiamide	210/212	151
Aneurine (vit. B_1)	245/250	Salophène	190	184
	232/237	Dicyandiamide	210/212	142
Riboflavine (vit. B_2)	282 déc.	Salophène	190	189
		Dicyandiamide	210/212	191
		Phénolphtaléine	263	248
Ac. L-Ascorbique	190/192	Benzanilide	163	159
		Salophène	190	174

ANALYSE D'UNE TACHE SUR PAPIER FILTRE

Un papier filtre porteur d'un produit organique peut facilement en être débarrassé par élution; après évaporation du solvant, le résidu est alors identifié. Si la substance organique est un acide aminé, il est plus facile et plus rapide de découper une fraction du papier chargé et de le soumettre à la sublimation en chambre humide, à basse température, que d'en faire une élution.

Le papier et l'acide aminé présumé sont déposés humectés, sur un porte-objet reposant sur le bloc chauffant[5] à une température comprise entre 100° et 200°. Le R_F de la tache fait présumer la présence d'un acide donné et d'après cela, la température à laquelle se poursuivra la sublimation, sera fixée. Un anneau de cuivre chauffé est ensuite placé autour de la tache et du papier, puis sur l'ensemble, est retourné un porte-objet chauffé, portant une goutte d'eau vers l'intérieur de la chambre. Au-dessus, à l'extérieur, se place un bloc de cuivre chauffé qui maintient tout au long de la sublimation une température favorable à la cristallisation des produits sublimés.

Après sublimation, le sublimat est mis dans une enceinte desséchante, avant de procéder aux déterminations d'indice ou d'eutectique. Lorsqu'il entre dans les intentions d'identifier par eutectique, la goutte d'eau placée au-dessus du papier contient en outre le cristal du partenaire eutectique choisi. Au cours de la sublimation, l'eutectique se forme — si eutectique il y a — à la surface du cristal du partenaire et on obtient ainsi une sorte de préparation de contact, très bien constituée. Il suffit alors après dessiccation, de gratter la préparation et d'observer la première fusion qui est toujours très facile à observer.

On obtient en une nuit, à 120°, une bonne sublimation d'acide glutamique. Les expériences faites à l'aide d'acide DL- et L- glutamique, et ensuite à l'aide de mélanges avec le DL- aspartique sont absolument démonstratrices. La température de fusion des eutectiques obtenus est bien la même que celle que l'on a observée avec les individus à l'état pur.

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TABLEAU VI

IDENTIFICATION DES ACIDES GLUTAMIQUES APRÈS SUBLIMATION

(Analyse d'une tache chromatographique sur papier)

Acides aminés contenus dans la tache sur le papier (µg)	*Partenaire eutectique µg*	*Sublimation T°*	*Durée*	*T° Fusion eutectique binaire observée*	*théorique*
Ac.DL-Glutamique (120 µg)	Ac.Oxalique (subl.) (120 µg)	120°	7 h	53/55/52 50/54 M/5 = 52° 8	50/52
id.	Dicyandiamide (120 µg)	120°	15 h	154/150 153/152 151/154 M/6 = 152° 3	150/152
id.	Ac. Oxalique (subl.) (120 µg)	120°	7 h	62/63/65 65/60/62 63/65/67 68 M/10 = 64°	64/65
id.	Dicyandiamide (120 µg)	120°	17 h	167/169 166/168 167 M/5 = 167° 4	166/167
Ac.DL-Glutamique (120 µg) Ac.DL-Aspartique (120 µg)	Dicyandiamide (30 µg)	120°	17 h	153/150 151/151 152/153 151/150 150/153 152 M/11 = 151° 4	150/152
Ac.DL-Glutamique (360 µg) Ac.DL-Aspartique (120 µg)	Dicyandiamide (30 µg)	120°	17 h	154/151 152/152 154/152 151/154 M/8 = 152°	150/152
Ac.DL-Glutamique (480 µg) Ac.DL-Aspartique (120 µg)	Dicyandiamide (30 µg)	120°	17 h	153/152 154/150 151/152 152/155 152/155 155/154 M/10 = 152° 8	150/152
Ac.L-Glutamique (120 µg) Ac.DL-Aspartique (120 µg)	Dicyandiamide (30 µg)	120°	19 h	165/167 167/164 166 M/5 = 166°	166/167

La dicyandiamide est préférable pour identifier de cette manière les acides glutamiques, parce qu'elle ne donne pas lieu à des phénomènes d'hydratation comme l'acide oxalique.

Cette même technique simple peut être étendue au contrôle de taches d'acides aminés simples, puisque tous subliment. Pour des taches globales, il serait nécessaire de développer l'étude des eutectiques ternaires. On peut compléter par la mesure de l'indice de réfraction pour reconnaître ces individus sublimés dans le mélange. Ceci s'appliquerait à l'analyse d'une tache chromatographique globale de phénylalanine, de leucine, d'*iso*leucine, et de norleucine.

Et comme indices et eutectiques sont affectés par l'isomérie (DL, L ou D) ces expériences peuvent renseigner sur la nature de l'isomère dans le mélange, renseignement que ne fournit pas le R_F.

CONCLUSION

La technique qui est préconisée ici pour l'analyse des taches d'acides aminés chromatographiés sur papier est basée sur la détermination des indices de réfraction et sur la température de fusion des eutectiques binaires. Les données qui servent de base à cette technique peuvent également servir au contrôle de pureté des individus isolés.

Elles permettent en effet de se rendre compte de la pureté isomérique, ce que ne fait pas la chromatographie.

Etant donné l'importance des acides aminés et des vitamines, il serait utile de poursuivre ces recherches.

Les indices de réfraction sont obtenus à ± 0.002 unités près et les fusions eutectiques à ± 1 à 2° près. La présence d'impureté peut être repérée selon le cas à partir de 1 à 3%. Tout dépend de l'allure des diagrammes thermiques des individus caractérisés avec leurs partenaires eutectiques.

RÉSUMÉ

L'indice de réfraction et la température de fusion eutectique de mélanges binaires, sont deux propriétés qui permettent une identification spécifique des individus et des isomères organiques. Elles ont été expérimentées à cet effet sur un certain nombre de vitamines et d'acides aminés. Il en résulte que l'analyse d'une tache globale d'acides aminés, sur papier devient facile grâce à ces propriétés. Un exemple relatif aux acides glutamiques, montre que cette analyse renseigne mieux que le R_F chromatographique sur la composition d'une tache globale sur papier.

SUMMARY

Refractive index and eutectic melting temperature of binary systems, together lead to specific identification of organic individuals and isomers. A number of vitamins and amino acids have been experimented with to that purpose. The result is that analysis of an entire spot of amino acids on paper becomes easy owing to these properties. An example using glumatic acids shows that better results on the composition of an entire spot on paper can be obtained by this analysis than by chromatographic R_F values.

ZUSAMMENFASSUNG

Der Brechungsexponent und die eutektische Schmelztemperatur von binären Gemischen, sind zwei Eigenschaften, welche eine spezifische Identifikation der organischen Körper und der Isomeren erlauben. Sie wurden zu diesem Zwecke an einer gewissen Anzahl Vitaminen und Aminosäuren ausprobiert. Daraus resultiert, dass die Analyse eines globalen Fleckens von Aminosäuren auf Papier, dank dieser Eigenschaften einfach wird. Ein Beispiel für die Glutaminsäuren zeigt, dass diese Analyse besser als der chromatographische R_F-Wert über die Zusammensetzung eines globalen Fleckens auf Papier Aufschluss gibt.

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DIETHYLENETETRA-AMMONIUM SULPHATOCERATE AS VOLUMETRIC REAGENT

I. IODINE MONOCHLORIDE METHOD

by

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The salts of quadrivalent cerium are the most versatile of the strong oxidizing agents, which may be used as standard solutions. Quadrivalent cerium salts are yellow and on reduction form trivalent colourless cerous salts. Cerate solutions are usually made up to approximately the concentration desired and then standardized with arsenious acid, sodium oxalate, ferrous ethylenediamine sulphate or electrolytic iron.

This paper describes the preparation of diethylenetetra-ammonium sulphatocerate, $[Ce(NH_2\text{–}CH_2\text{–}CH_2\text{–}NH_2)_2](SO_4)_2.2H_2SO_4.7H_2O$, and its use as an oxidimetric standard in volumetric analysis.

In the presence of hydrochloric acid, diethylenetetra-ammonium sulphatocerate has been used as a volumetric reagent for the determination of potassium iodide, ferrous ammonium sulphate, arsenious oxide, stannous chloride, hydrazine sulphate, thallous chloride, hydroquinone and potassium ferrocyanide.

Preparation of diethylenetetra-ammonium sulphatocerate

Ceric sulphate (E. Merck) and ethylenediamine hydrate (E. Merck) in equimolecular proportions were dissolved in $2N$ and $4N$ sulphuric acid respectively. The two solutions were mixed together, concentrated and allowed to stand overnight, when deep orange coloured crystals were formed. These crystals were filtered on a Buchner funnel, washed thoroughly with absolute alcohol and dried in an electric oven at 60° C. A sample of diethylenetetra-ammonium sulphatocerate was analysed and found to contain Ce, 18.09%; C, 6.19%; N, 7.20%; S, 16.52%. The calculated values for the formula, $[Ce(NH_2\text{–}CH_2\text{-}CH_2\text{–}NH_2)_2]\ (SO_4)_2.\ 2H_2SO_4.7H_2O$, are Ce, 18.09%; C, 6.20%; N, 7.23%; S, 16.56%.

Diethylenetetra-ammonium sulphatocerate prepared by this method showed no tendency to undergo any decomposition, deliquescence or efflorescence. A sample of this compound left loosely covered in the laboratory for about six months showed no change in composition. The compound is easy to prepare and preserve in the pure state. Its solution may be heated to boiling without decomposition. As an oxidant it has a high molecular or equivalent weight (774.7).

EXPERIMENTAL

A known amount of each substance was transferred to a conical flask and about 25 ml of water, 50 ml of concentrated hydrochloric acid, 5 ml of 0.01*M* iodine monochloride and 5 ml of chloroform were added. The mixture was cooled to room temperature and titrated against standard diethylenetetra-ammonium sulphatocerate. The reagent was added from a burette until the solution, which was coloured with iodine, became pale yellow and the chloroform layer acquired a purple colour due to iodine. The conical flask was stoppered and vigorously shaken during the titration. Addition of small volumes of the sulphatocerate solution was continued, shaking vigorously after each addition until the chloroform layer was faintly violet. The sulphatocerate was then added dropwise, with shaking after the addition of each drop, until the chloroform layer became very pale yellow. The end-point was very sharp.

The standard solution of diethylenetetra-ammonium sulphatocerate was prepared by dissolving its known weight in 2*N* sulphuric acid solution and making up to a known volume with the acid. In these titrations normality of the solution with respect to hydrochloric acid was kept between 5*N* to 7*N*. Several titrations were performed in each case. From the volume of the sulphatocerate used, corresponding to the end-point in each titration, the amount of each substance was calculated. From the results given in Tables I-VIII it may be concluded that diethylenetetra-ammonium sulphatocerate (DTS) is an oxidimetric standard for the determination of potassium iodide, ferrous ammonium sulphate, arsenious oxide, stannous chloride, hydrazine sulphate, thallous chloride, hydroquinone and potassium ferrocyanide.

TABLE I

POTASSIUM IODIDE ($I^- \rightarrow I^+$)

KI taken *g*	*0.02N DTS used* *ml*	*KI found* *g*
0.0154	9.30	0.0154
0.0199	12.00	0.0199
0.0257	15.50	0.0257
0.0299	18.00	0.0299
0.0352	21.20	0.0352

TABLE II

FERROUS AMMONIUM SULPHATE ($Fe^{+2} \rightarrow Fe^{+3}$)

$FeSO_4.(NH_4)_2SO_4.6H_2O$ *taken g*	*0.02N DTS used ml*	$FeSO_4.(NH_4)_2SO_4.6H_2O$ *found g*
0.0510	6.50	0.0510
0.0729	9.30	0.0729
0.0941	11.95	0.0937
0.1113	14.15	0.1110
0.1330	16.95	0.1329

TABLE III

ARSENIOUS OXIDE ($As^{+3} \rightarrow As^{+5}$)

As_2O_3 *taken* *g*	*0.02N DTS used* *ml*	As_2O_3 *found* *g*
0.0109	11.00	0.0109
0.0132	14.35	0.0132
0.0168	17.05	0.0169
0.0201	20.30	0.0201
0.0228	23.00	0.0228

TABLE IV

STANNOUS CHLORIDE ($Sn^{+2} \rightarrow Sn^{+4}$)

$SnCl_2.2H_2O$ *taken* *g*	*0.02N DTS used* *ml*	$SnCl_2.2H_2O$ *found* *g*
0.0181	8.00	0.0181
0.0280	12.35	0.0279
0.0338	15.00	0.0338
0.0406	17.95	0.0405
0.0474	20.95	0.0473

TABLE V

HYDRAZINE SULPHATE ($N_2H_4 \rightarrow N_2 + 4H^+$)

$N_2H_4.H_2SO_4$ *taken* *g*	*0.02N DTS used* *ml*	$N_2H_4.H_2SO_4$ *found* *g*
0.0049	7.50	0.0049
0.0074	11.25	0.0073
0.0105	16.15	0.0105
0.0128	19.70	0.0128
0.0143	22.00	0.0143

TABLE VI

THALLOUS CHLORIDE ($Tl^+ \rightarrow Tl^{+3}$)

TlCl taken *g*	*0.02N DTS used* *ml*	*TlCl found* *g*
0.0240	10.00	0.0240
0.0288	12.00	0.0288
0.0384	16.00	0.0384
0.0504	21.00	0.0504
0.0576	24.00	0.0576

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TABLE VII

HYDROQUINONE ($C_6H_4(OH)_2 \rightarrow C_6H_4O_2 + 2H^+$)

$C_6H_4(OH)_2$ *taken* g	0.02*N DTS used* ml	$C_6H_4(OH)_2$ *found* g
0.0091	8.25	0.0091
0.0129	11.65	0.0128
0.0185	16.80	0.0185
0.0211	19.15	0.0211
0.0259	23.40	0.0258

TABLE VIII

POTASSIUM FERROCYANIDE

($[Fe(CN)_6]^{-4} \rightarrow [Fe(CN)_6]^{-3}$)

$K_4[Fe(CN)_6]$ *taken* g	0.02*N DTS used* ml	$K_4[Fe(CN)_6]$ *found* g
0.0591	7.00	0.0591
0.1014	12.05	0.1017
0.1309	15.50	0.1309
0.1605	19.00	0.1605
0.1858	22.05	0.1862

SUMMARY

The method of preparation of diethylenetetra-ammonium sulphatocerate is described. This substance has been used as an oxidant to determine potassium iodide, ferrous ammonium sulphate, arsenious oxide, stannous chloride, hydrazine sulphate, thallous chloride, hydroquinone and potassium ferrocyanide by a volumetric method, using iodine monochloride as catalyst and pre-oxidizer. During these titrations, normality of the solution with respect to hydrochloric acid has been kept at about 6*N*. Chloroform is used as an indicator. It is coloured pink owing to the liberation of iodine during the titration and becomes very pale yellow at the end-point because of the formation of iodine monochloride.

RÉSUMÉ

Une méthode de préparation du sulfate de di(éthylènediamino)-cérium(IV) est décrite. Le réactif a été utilisé comme oxydant pour le dosage de l'iodure de potassium, du sulfate de fer(II) et d'ammonium, de l'anhydride arsénieux, du chlorure d'étain(II), du sulfate d'hydrazine, du chlorure de thallium(I), de l'hydroquinone et du ferrocyanure de potassium par volumétrie, en présence de monochlorure d'iode comme catalyseur et pré-oxydant. Pendant ces titrations, la normalité de la solution en acide chlorhydrique est maintenue à 6. Le chloroforme est utilisé comme indicateur. Il se colore en violet par l'iode libéré durant le titrage et devient jaune très pâle au point final, par formation de monochlorure d'iode.

ZUSAMMENFASSUNG

Die Autoren beschreiben eine Methode zur Darstellung von Cer(IV)di(äthylendiamin) sulfat. Das Reagenz wird, in Gegenwart von Jodmonochlorid als Katalysator und voroxydierendes Mittel, als Oxydationsmittel zur volumetrischen Bestimmung folgender Substanzen verwendet: Kaliumjodid, Eisen(II)sulfat, Ammoniumsulfat, arsenige Säure, Zinn(II)chlorid, Hydrazinsulfat, Thallium(I)chlorid, Hydrochinon, Kaliumferrocyanid. Während dieser Titrationen wird die Normalität der Salzsäurelösung bei sechs konstant gehalten. Das Chloroform wird als Indikator benützt. Es färbt sich violett durch das während der Titration freigewordene Jod und wird am Endpunkt blass gelb durch die Bildung von Monochlorid.

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FLUOROBERYLLATES IN CHEMICAL ANALYSIS

by

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Extensive work of RAY and his co-workers[1] showed close analogy between sulphates and fluoroberyllates. RAY[2] showed that barium fluoroberyllate, having the composition $Ba[BeF_4]$, is insoluble in water and in dilute acids and has the same crystal structure as barium sulphate.

An investigation was made of the use of a soluble fluoroberyllate as precipitating agent in the quantitative estimation of barium. This was done in order to study the analogy of sulphates and fluoroberyllates in their analytical reactions and not with any intention of replacing sulphates by fluoroberyllates in conventional analysis.

It was decided from the beginning to use a neutral solution for precipitation to avoid platinum vessels. With neutral solution sintered glass crucibles can be used for filtration.

Preliminary experiments to precipitate a neutral barium chloride solution by ammonium fluoroberyllate solution gave low results due to some co-precipitated barium fluoride. The fluoride ion was furnished by dissociation of the fluoroberyllate.

In presence of ethylenediaminetetraacetic acid (complexone) barium fluoride does not precipitate in neutral solution though barium fluoroberyllate does precipitate. Under these conditions lead does not precipitate and a separation of barium and lead can be achieved.

PRIBIL AND MARICOVA[3] separated barium from lead and many other elements by precipitating barium sulphate in presence of complexone. Barium sulphate dissolves in ammoniacal complexone solution from which it can be reprecipitated by acidification. Barium fluoroberyllate on treatment with ammoniacal complexone solution partially hydrolyzed to beryllium hydroxide and therefore pure barium fluoroberyllate could not be reprecipitated on acidification.

Reagents and chemicals

1. Complexone — disodium ethylenediaminetetraacetic acid A.R. 10% solution was used.
2. Ammonium fluoroberyllate — recrystallized ammonium fluoroberyllate prepared according to the method of RAY. 10% solution was used.
3. Barium chloride stock solution prepared from A.R. quality barium chloride. Strength determined gravimetrically as barium sulphate.
4. Lead nitrate stock solution — prepared from A.R. quality lead nitrate. Strength determined gravimetrically as lead sulphate.

All other reagents were A.R. grade.

Procedure

The acidic solution containing barium was treated with 10 ml complexone diluted to 200 ml and adjusted to pH 6 with dilute ammonium hydroxide, methyl red being used as indicator. The solution was heated to boiling and 10 ml of ammonium fluoroberyllate solution was added dropwise with constant stirring. The solution was allowed to stand on a hot plate for few minutes, cooled to room temperature, filtered through a sintered glass crucible and washed thoroughly with cold water. The precipitate was dried at 110° C and weighed as $BaBeF_4$ — containing 61.765% barium. The results are shown in Table I.

TABLE I

Barium present mg	*Ba[BeF$_4$] precipitated* mg	*Barium found* mg	*Error* mg
27.32	44.3	27.36	+0.04
27.32	44.2	27.30	−0.02
40.98	66.5	41.04	+0.06
40.98	66.6	41.03	+0.05
54.64	88.5	54.66	+0.02
54.64	88.6	54.73	+0.09
68.30	110.6	68.31	+0.01
68.30	110.4	68.20	−0.10

The same procedure was adopted for separation of barium from lead. Results are given in Table II.

TABLE II

Barium present mg	*Lead present* mg	*Barium found* mg	*Error* mg
68.30	6.96	68.31	+0.01
68.30	6.96	68.31	+0.01
68.30	34.81	68.20	−0.10
68.30	34.81	68.20	−0.10
68.30	69.62	68.20	−0.10
68.30	69.62	68.20	−0.10
68.30	139.24	68.20	−0.10
68.30	139.24	68.31	+0.01
68.30	696.2	68.31	+0.01
68.30	696.2	68.20	−0.10

The crucibles were cleaned by heating with a mixture of boric acid and hydrochloric acid.

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SUMMARY

Barium can be precipitated as barium fluoroberyllate, $Ba[BeF_4]$, with ammonium fluoroberyllate in the presence of ethylenediaminetetraacetic acid at pH 6-7. Lead does not precipitate under these conditions and a good separation can be effected. The precipitate is dried at 110° C and weighed.

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RÉSUMÉ

Le baryum peut être précipité comme fluoglucinate $Ba[BeF_4]$, au moyen de fluoglucinate d'ammonium, en présence d'acide éthylènediaminetétraacétique, au pH 6-7. Le plomb ne précipite pas dans ces conditions, ce qui permet une bonne séparation baryum-plomb. Le précipité obtenu est séché à 110° C et pesé.

ZUSAMMENFASSUNG

Das Barium kann als Fluoroglucinat $Ba[BeF_4]$ mittels Ammonium-Fluoroglucinat, in Gegenwart von Äthylendiamintetraessigsäure bei pH 6-7 ausgefällt werden. Das Blei fällt unter diesen Bedingungen nicht aus, was eine gute Trennung Blei-Barium erlaubt. Der erhaltene Niederschlag wird bei 110° getrocknet und gewogen.

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OPRECIPITATION OF COBALT WITH NICKEL DIMETHYLGLYOXIME

by

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INTRODUCTION

In 1905, Tschugaeff[1] discovered that dimethylglyoxime reacts with the nickel(II) on to give a brilliant red insoluble compound. His work was verified and extended y Kraut[2], who showed that as little as one microgram of nickel could be detected y this reaction. The use of dimethylglyoxime for the gravimetric determination f nickel was first proposed by Brunck[3], who investigated the completeness of recipitation both from ammoniacal solution and from solutions buffered with the cetate ion. Since these early investigations, many modifications have been proposed, ost of them dealing with methods to prevent the coprecipitation of other metal ons[4,5]. The red precipitate formed by the reaction of dimethylglyoxime with nickel on has been shown to have a composition $Ni(C_4H_7O_2N_2)_2$. Other investigators have hown that the compound is a planar first order inner complex[4].

Almost without exception, articles in the literature appear to agree that dimethyl- lyoxime will completely separate nickel from cobalt under proper conditions[5]. It has een reported that when large amounts of nickel are precipitated in the presence of mall amounts of cobalt, the precipitation with dimethylglyoxime from an ammoniacal olution gives a clean separation. Most authors agree that when cobalt is present an xcess of dimethylglyoxime sufficient to complex all the cobalt must be added[4]. Brunck ecommended an amount of dimethylglyoxime about five times the amount of ickel present with no mention of any relation to the quantity of cobalt present[7].

Large amounts of cobalt and copper seem to retard the precipitation of nickel limethylglyoxime, but the difficulty may be overcome by using excess dimethylgly- xime and by allowing extra time for precipitation[8]. In ammoniacal solution, the obalt dimethylglyoxime complex appears to retard the precipitation of small amounts f nickel[5], but this difficulty can be avoided by using the acetate method[6,8,9]. The ickel precipitate is also often peptized by the cobalt complex, making filtration lifficult[5]. Macro amounts of nickel have been precipitated from homogeneous solution ontaining dimethylglyoxime and urea. Hydrolysis of the latter compound was mployed to adjust the pH value.

The cobalt(II)-dimethylglyoxime complex has been characterized by the method f continuous variations, which indicated that there is a cobalt-to-dimethylglyoxime atio of 1:2 [12]. Since the cobalt complex is soluble, it is probably a second order complex. CAMBI AND CORISELLI state that cobalt(II) goes over very readily to cobalt(III) in the presence of dimethylglyoxime[13]. Many complexes, some soluble, some insoluble, have been identified following the oxidation of cobalt(II) to cobalt(III) in the presence of dimethylglyoxime and air[13].

In this work it was proposed to investigate the coprecipitation of cobalt with nickel in the various dimethylglyoxime procedures when the cobalt is present in small amounts. The determination of the cobalt was to be facilitated by labeling it with its radioisotope cobalt-60.

EXPERIMENTAL

Chemicals and apparatus

Five millicuries of cobalt-60 as 3.1 mg of cobalt(II) chloride was obtained from Oak Ridge National Laboratory. This was used to prepare 50 ml of a standard solution containing 6.12 mg of cobalt per ml in the form of cobalt(II) sulfate. The gamma ray radioactivities of various cobalt-60-containing solutions were measured in a specially designed glass sample holder with a volume of 15 ml. This holder was placed in constant geometry near a Model SC-1B Nuclear Research Corporation Scintillation Counter which was attached to a conventional scaler and timer.

Jacketed beakers, with constant-temperature water flowing through the jackets, were used for all precipitations. The temperature control was in all cases within ±2°. Samples were stirred with magnetic stirrers.

The nickel solution used in all precipitations was one of nickel(II) sulfate containing 5.76 mg of nickel per ml. The dimethylglyoxime solution was prepared by dissolving 7.5 g of the reagent grade material in 1 l of 95% ethanol. All other chemicals were of reagent grade quality.

The ammonia method

Ten ml of the nickel sulfate solution (57.6 mg of nickel), 0.1 ml of radioactive cobalt sulfate solution (612 μg of cobalt), and 10 ml of distilled water were placed in the beaker for each determination. Rapid addition studies were made by dumping 40 ml of the dimethylglyoxime solution and 5 ml of concentrated ammonium hydroxide into the solution. These studies were carried out at 25° and at 85°. Slow addition studies were made by adding 40 ml of the dimethylglyoxime to the solution followed by 5 ml of concentrated ammonium hydroxide added dropwise at the rate of 1 drop per sec, the latter addition bringing about the precipitation.

Following addition of the reagents, the precipitates were digested for various times. They were then separated by filtration, dissolved in concentrated hydrochloric acid, diluted to 25 ml total volume, and 15 ml was placed in the sample holder and counted. Comparison with a standard cobalt sample allowed the amount of coprecipitated cobalt to be calculated. The filtrates from the precipitations were all tested for completeness of precipitation by the use of a large excess of ammonia and dimethylglyoxime solutions.

The acetate method

The same conditions as to the amounts of nickel, cobalt and dimethylglyoxime, mode of reagent addition, and treatment of the samples after precipitation prevailed during the acetate precipitations as during those in ammoniacal media. However, instead of ammonium hydroxide, 15 ml of 10% sodium acetate solution was added, followed by 1 g of solid sodium acetate.

Results

For each determination at a given temperature, addition time, and digestion time, at least five runs were made. The average of these runs was determined and the standard deviation of the average was calculated. The result of each determination was expressed as the average with the reliable error (90% confidence level[14]) affixed. In all cases of rejected data, the method of PIERCE AND CHAUVENET[15] was the basis. Tables I and II present the results obtained in the ammonia method, and Tables III and IV present those obtained by the acetate method.

TABLE I

COBALT COPRECIPITATED WITH $Ni(dmg)_2$ BY THE AMMONIA METHOD AT 25°

Reagent addition	*Digestion (min)*	*Cobalt (μg)*
slow	0	26.6 ± 7.9
slow	30	2.6 ± 1.3
rapid	0	52.2 ± 9.9
rapid	30	8.9 ± 4.4
rapid	90	4.6 ± 2.0
rapid	180	2.6 ± 2.1
rapid	300	2.9 ± 1.1

TABLE II

COBALT COPRECIPITATED WITH $Ni(dmg)_2$ BY THE AMMONIA METHOD AT 85°

Reagent addition	*Digestion (min)*	*Cobalt (μg)*
slow	0	4.6 ± 3.1
slow	30	5.9 ± 2.7
rapid	0	4.1 ± 3.0
rapid	30	4.5 ± 2.2
rapid	60	5.3 ± 2.3
rapid	120	11.2 ± 3.6
rapid	210	11.3 ± 3.8
rapid	300	20.8 ± 2.1

TABLE III

COBALT COPRECIPITATED WITH $Ni(dmg)_2$ BY THE ACETATE METHOD AT 25°

Reagent addition	*Digestion (min)*	*Cobalt (μg)*
slow	0	7.1 ± 2.3
slow	30	5.3 ± 3.1
rapid	0	14.0 ± 1.6
rapid	30	2.9 ± 2.5
rapid	60	7.5 ± 1.5
rapid	120	10.8 ± 1.9
rapid	210	7.0 ± 1.5
rapid	300	6.9 ± 3.9

TABLE IV

COBALT COPRECIPITATED WITH $Ni(dmg)_2$ BY THE ACETATE METHOD AT 85°

Reagent addition	*Digestion (min)*	*Cobalt (μg)*
slow	0	4.6 ± 1.9
slow	30	16.1 ± 4.0
rapid	0	5.0 ± 2.5
rapid	30	14.1 ± 4.2
rapid	60	17.9 ± 1.7
rapid	120	17.1 ± 4.8
rapid	210	128.0 ± 10.9
rapid	300	125.0 ± 12.4

DISCUSSION

The amount of cobalt coprecipitated with the nickel dimethylglyoxime by the ammonia method at 25° is very large for the determinations (both slow and rapid) in which the precipitates were not digested after addition of the reagents. However, as the digestion time increased, the carried cobalt decreases to an almost constant amount. The precipitates which were not stirred after completion of the precipitation were gelatinous and difficult to filter, but with longer stirring times the material became more curdy or mealy, and consequently it was much easier to filter. The relatively large amount of cobalt coprecipitated initially is believed to be due to a trapping process and to adsorption on the large surface area presented by the gelatinous precipitate. With longer digestion times, the precipitate reforms, probably through the process of Ostwald ripening, releasing the trapped cobalt, and also decreasing the surface area[16]. It is possible that the small amount of cobalt which could not be removed even by prolonged digestion was in solid solution with the nickel dimethylglyoxime, the cobalt occupying sites which would ordinarily be occupied by nickel. The formation of such a solid solution might be easy since the cobalt(II) complex may be similar to that of nickel[12,13,17,18,19].

The coprecipitation of cobalt in the ammonia method at 85° shows a constant increase in the amount of cobalt as the digestion time increases. As the precipitate formed, it was gelatinous, but it became mealy very quickly (within one minute after the addition of the reagents). Then as time went on, the small mealy clumps gathered into larger more slimy looking aggregates, the size growing as the time increased. It is believed that no initially high value for coprecipitated cobalt was observed because the transformation from gelatinous to mealy precipitate occurred before separation of the solution and precipitate could be effected. The increase in carried cobalt with time, as well as the change in form of the precipitate may be related to the loss of alcohol at this temperature, and the resulting decrease in the solubility of dimethylglyoxime.

The initially high value of coprecipitated cobalt in the acetate method at 25° may again be related to the character of the precipitate, which was very gelatinous at the beginning. With increased digestion time the precipitate became mealy, the clump size remaining fairly constant. The decrease in cobalt coprecipitated with increased digestion time could again be explained by this transformation in the appearance of the precipitate. There seems to be no obvious explanation for the later rise and subsequent drop in the amount of cobalt carried as the digestion time goes from 60 to 300 minutes. This behavior may be related to a valence change of cobalt from (II) to (III) and/or a change in the form of the cobalt dimethylglyoxime complex. CAMBI AND CORISELLI state that cobalt(II) goes to cobalt(III) quite easily under these conditions[13]. Numerous complexes of cobalt(III) with dimethylglyoxime have been reported; some are insoluble, which might alter the coprecipitation picture markedly[13,17,18,19].

Initially the amount of cobalt brought down by the acetate method at 85° is relatively small. However, as time goes on, this amount increases, reaching a very high value after 120 minutes. An explanation similar to that given in the ammonia procedure at 85° would seem to be applicable here. Valence changes such as those postulated in the previous paragraph may have occurred; if they did, however,

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their effects could have been masked by the rapid rise in coprecipitation produced by the precipitate form at this temperature.

In all cases, the effect of slow reagent addition was to accelerate the phenomena which would occur in the rapid addition procedure. Of those investigated, the best condition for the precipitation of nickel in the presence of small amounts of cobalt by the dimethylglyoxime method seems to be the slow addition of ammonia followed by a digestion for 30 minutes, all processes being carried out at 25°.

SUMMARY

The coprecipitation of cobalt with nickel precipitated as the dimethylglyoxime complex has been investigated under various conditions. Precipitations were carried out in ammonia and acetate solutions, at 25° and 85°, with slow and rapid addition of the solution of the precipitating agent, and with various digestion times. In each experiment, the amount of cobalt was 612 μg and the amount of nickel was 57.6 mg. Of the methods investigated, minimum coprecipitation was achieved by slow addition of ammonia to the acid nickel, cobalt, and dimethylglyoxime solution followed by a 30-minute digestion, all processes being carried out at 25°.

RÉSUMÉ

La coprécipitation du cobalt avec le complexe nickel-diméthylglyoxime a été examinée dans diverses conditions. Les précipitations ont été effectuées en solutions ammoniacales et d'acétate, à 25 et 85°, avec additions lente et rapide de la solution de réactif et avec des digestions de différentes durées. Pour chaque expérience, la teneur en cobalt était de 612 μg et la teneur en nickel de 57.6 mg. On a trouvé que la coprécipitation était la plus faible dans les conditions suivantes: addition lente d'ammoniaque à la solution acide de nickel, cobalt et diméthylglyoxime, suivie d'une digestion de 30 minutes; température de 25° pour toutes les opérations.

ZUSAMMENFASSUNG

Die Kopräzipitation von Kobalt mit dem Komplex Nickel-Dimethylglyoxim wurde unter verschiedenen Bedingungen untersucht. Die Ausfällungen wurden bei 25 und 85° in Ammoniak- und Acetatlösungen ausgeführt mit langsamer und schneller Zugabe der Reagenzlösung und mit Wartezeiten von verschiedener Dauer. Für jedes Experiment war der Gehalt an Kobalt 612 μg und der Gehalt an Nickel 57.6 mg. Man fand, dass die Kopräzipitation unter folgenden Bedingungen am schwächsten war: langsame Zugabe von Ammoniak zu der sauren Lösung von Nickel, Kobalt und Dimethylglyoxim, bei nachheriger Wartezeit von 30 Minuten, Temperatur 25° für alle Operationen.

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SEPARATION OF CALCIUM AND ALUMINUM FROM IRON BY AN ION EXCHANGE METHOD

by

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INTRODUCTION

A method has been worked out for the determination of calcium and aluminum in the presence of iron. Calcium is separated from iron and aluminum by means of an anion exchanger according to the method devised by SAMUELSON, LUNDÉN, AND SCHRAMM[5]. Iron and aluminum are, provided that proper conditions are chosen, taken up quantitatively in a column filled with a resin in the citrate form. Calcium passes into the effluent. The separation of aluminum from iron is based upon the pioneering work by KRAUS AND MOORE[3] on the behavior of different metal ions in concentrated hydrochloric acid. These authors found that in strong hydrochloric acid iron is bound very strongly to an anion exchanger in chloride form whereas aluminum is easily eluted.

In the present work it is shown that the citrate ions left in the column after the removal of the calcium ions do not interfere with the separation of aluminum from iron by elution with concentrated hydrochloric acid. Special precautions have to be taken to obtain a quantitative separation.

The method has been adopted for the analysis of commercial products, *e.g.* lime.

EXPERIMENTAL PART

Ion exchange column

A modified type of ion exchange column used in the present investigation is shown in Fig. 1. This type of column permits the introduction of the elutriant at the bottom of the column through the three-way cock. In other respects the column is of standard type and filled with resin in the usual manner[4].

The strongly basic anion exchanger Dowex 2 was used in all experiments. The particle size was 0.2-0.3 mm and the dimensions of the resin bed 15 × 180 mm. The resin was transformed into the citrate form by passing 300 ml 1M citric acid through the column and washing with about 200 ml water. It must be observed that the method does not work when weakly basic resins are used and that aluminum and iron are not taken up quantitatively on a strongly basic anion exchanger if the resin contains a considerable number of weakly basic groups.

Ion exchange procedure

The solution to be analysed is introduced into the funnel A and passed downwards through the resin bed and through the outlet tube B. After washing with water until no calcium ions appear in the effluent, calcium is determined in the collected effluent and washing water. A proper flow rate in both these steps is 2 ml/min. In the experiments performed in the present investigation it was found that about 300 ml water was required in the washing step. It has, however, been observed that different resins of similar quality behave somewhat differently and it is therefore recommended to work with a broad margin of safety and to make control tests when new resins are used. As the distilled water contained traces of impurities the water was deionized before use[4].

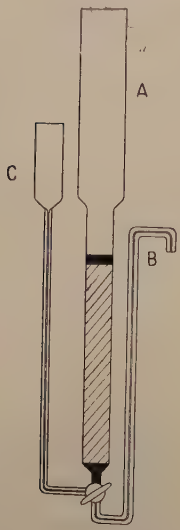

Fig. 1. Ion exchange column.

After the sorption step the funnel C is filled with concentrated hydrochloric acid and, by switching the three-way cock, the acid is forced upwards through the resin bed. In this manner the water left in the column is displaced from the column into the funnel A. Iron and aluminum are to a large extent removed from the column. The solution which appears in the funnel A has a yellow color due to the iron chloride complex.

It must be noted that the glass tube which connects the funnel C with the three-way stopcock must be filled with solution in order to prevent air being forced into the column. If the tube is a capillary it can be simply filled by switching the cock to connect the capillary with the outlet tube and applying gentle suction.

A further amount of concentrated acid (about 75 ml) is placed in the funnel A in such a way that mixing occurs. The cock is switched over to the same position as that during the sorption step and the hydrochloric acid is passed downwards through the resin bed. Iron is readsorbed in the column and the eluate which contains the aluminum is taken out through the outlet tube B. The solution is displaced by means of concentrated hydrochloric acid until aluminum has been eluted quantitatively. About 75 ml is required under the conditions used in the present work. Iron can be eluted by washing with water and 1 M hydrochloric acid.

It can be mentioned that some modifications in the elution of aluminum have been tried but the method described above is considered to be the simplest.

Analytical methods

In the experiments with mixtures of pure salt solutions, the solutions of calcium chloride, magnesium chloride, and manganese chloride were standardized by gravimetric determinations as sulfate. Aluminum was determined by precipitation with 8-hydroxyquinoline.

Calcium, which was obtained after the sorption step in the effluent, was determined as sulfate after ignition to remove citric acid, addition of sulfuric acid, and heating at 700° C[5]. In some experiments with solutions which in addition contained magnesium and manganese, the sum was determined as sulfate. When manganese was present, the ash was treated with hydrogen peroxide after the ignition and addition of sulfuric acid in order to reduce manganese to the bivalent state.

Aluminum was determined in the eluate after addition of sulfuric acid, evaporation and ignition to remove citric acid. The ash was dissolved by melting with potassium hydrogen sulfate and aluminum determined gravimetrically as oxinate[3].

For a comparison and control of the analyses of lime, aluminum and iron have been determined colorimetrically with ferron[1] and the sum by precipitation as hydroxide. In the lime analysis, 2-3 g lime was treated with 15 ml water and stirred thoroughly to wet the powder. It was then treated with 20 ml of concentrated hydrochloric acid and evaporated to dryness with an infrared lamp. After heating for one hour at 185° C, the sample was dissolved in hydrochloric acid and silica removed by filtration in the usual manner. After washing, the filtrate was evaporated to dryness on a water bath. The residue was dissolved in water and 5 ml 1 M hydrochloric acid added to complete dissolution. The solution was diluted to 250 ml and 20 ml taken for each determination. A large excess of acid has to be avoided[5].

RESULTS AND DISCUSSION

The results from experiments performed with solutions to which known amounts of calcium chloride, aluminum chloride, and iron chloride had been added are given in Table I. In some of the solutions, magnesium chloride and manganese chloride were also present. As may be seen from the table, calcium is recovered quantitatively

TABLE I

ANALYSIS OF SOLUTIONS CONTAINING KNOWN AMOUNTS OF Ca, Mg, Mn, Al, AND Fe

Added					Found			
					Ca + Mg + Mn		*Al*	
Fe mmol	*Ca mmol*	*Mg mmol*	*Mn mmol*	*Al mmol*	*mmol*)*	*rel. error %*	*mmol*	*rel. error %*
0.5	4.985			0.497	4.981	−0.1	0.496	−0.2
0.5	1.621			0.499	1.617	−0.2	0.498	−0.2
0.5	1.621			0.499	1.614	−0.4	0.497	−0.4
0.5	3.988			0.497	3.987	0.0	0.497	0.0
0.5	1.994			0.497	1.992	−0.1	0.498	+0.2
0.5	5.982			0.497	5.976	−0.1	0.495	−0.4
0.5	2.991			0.199	2.990	0.0	0.200	+0.5
0.5		2.002		0.497	2.006	+0.2	0.497	0.0
0.5		3.003		0.497	3.004	0.0	0.495	−0.4
0.5		4.004		0.497	4.001	−0.1	0.495	−0.4
0.5	2.991	3.003		0.497	6.003	+0.2	0.496	−0.2
0.5	2.991		0.500	0.100	3.500	+0.3	0.100	0.0
0.1	5.982		0.050	0.199	6.024	−0.1	0.200	+0.5
0.1	5.982		0.050	0.050	6.030	0.0	0.050	0.0

* For the samples which contain Mg or Mn as well as Ca, these values are calculated from the weight of the sulfates using an average molecular weight calculated from the composition of the sample.

in the effluent from the column. Magnesium and manganese are also quantitatively recovered. The maximum relative error is 0.4%. The separation of aluminum from iron by elution with hydrochloric acid is also excellent. The greatest difference between the added and found amounts of aluminum is 0.002 mmol and the maximum relative error 0.5%. In separate experiments, colorimetric tests were used to check that no iron appeared in the eluate. It was found that less than 10^{-4} mmol iron was present in the eluate.

Aluminum has been determined in four different samples of burnt lime. The proposed ion exchange method has been compared with the usual difference method in which the sum of Al_2O_3 and Fe_2O_3 is determined by precipitation with ammonia and Fe_2O_3 colorimetrically. Furthermore, determinations of aluminum have been performed according to the direct spectrophotometric method with ferron[1]. The same reagent has been used in the colorimetric determination of iron. The results are given in Table II. The results from the gravimetric determination of silica and the determination of calcium plus magnesium (calculated as CaO) according to the ion exchange method are included in the table.

TABLE II

ANALYSIS OF BURNT LIME

SiO_2 % *gravim.*	*CaO % ion exchange*	$Al_2O_3 + Fe_2O_3$ % *gravim.*	Fe_2O_3 % *ferron*		Al_2O_3 % *by difference*	Al_2O_3 % *ferron*		Al_2O_3 % *ion exchange*	
1.84	94.6	0.49	0.17	0.18	0.31	0.28	0.31	0.25	0.26
1.55	92.2	0.62	0.19	0.18	0.43	0.43	0.43	0.42	0.40
1.84	93.3	0.61	0.20	0.23	0.39	0.42	0.36	0.38	0.37
2.67	91.9	0.75	0.24	0.32	0.48	0.43	0.46	0.41	0.42

As can be seen from the table, the proposed ion exchange method gives reproducible results for Al_2O_3 also in samples containing a large excess of calcium. The agreement between the three methods is rather satisfactory. The accuracy of the ion exchange method can be increased by using larger samples but this will of course make the operation more time-consuming.

It can also be mentioned that the method has been used for the determination of aluminum in silica, which contained in addition sodium, calcium, and iron. In two analyses, the ion exchange method gave 2.60% and 2.61% Al_2O_3 whereas the difference method gave 2.65% and 2.67%. In this case iron was determined by permanganate titration. It is believed that the proposed ion exchange method is more accurate as it is difficult to remove the last traces of silica which interfere in the difference method.

From the data presented above, it is obvious that the proposed ion exchange method can be used to advantage for the determination of aluminum, calcium, and magnesium in the presence of iron. Manganese behaves in the same manner as calcium and magnesium and does not interfere with the determination of aluminum. In samples containing considerable amounts of iron and aluminum, the proposed procedure seems to be more accurate than the methods generally used at present. The method is also applicable when only small amounts of iron and aluminum are present. As in most other applications of the ion exchange technique the proposed procedure is well suited for routine analyses as several columns can be operated simultaneously. The separation of the sample into three groups, (a) calcium, magnesium, and manganese, (b) aluminum, (c) iron, requires about 4 hours, the time for regeneration of the column not being included.

In the present investigation, most work has been devoted to the determination of aluminum after the separation from iron, calcium, magnesium, and manganese. The separation of calcium and magnesium from iron, aluminum and also other metals by the citrate form of an anion exchanger has been dealt with in detail in the earlier paper[5]. Instead of the gravimetric determination of calcium and magnesium as sulfate after the ion exchange separation from iron and aluminum, other gravimetric or titrimetric methods can of course be used.

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SUMMARY

An ion exchange method has been worked out for the separation of calcium and aluminum from iron. In the first step iron and aluminum are taken up in a column filled with an anion exchanger in the citrate form, whereas calcium passes into the effluent. Subsequently, aluminum is eluted by means of concentrated hydrochloric acid.

The method has been adapted to the analysis of lime.

RÉSUMÉ

Une méthode par échange d'ions a été établie pour la séparation du calcium et de l'aluminium du fer. Le fer et l'aluminium sont d'abord retenus sur une colonne remplie avec un échangeur d'anions, sous forme de citrates, tandis que le calcium passe dans l'éluat. L'aluminium est élué par l'acide chlorhydrique concentré.

Cette méthode a été appliquée à l'analyse de la chaux.

ZUSAMMENFASSUNG

Eine Ionenaustauschmethode für die Trennung von Calcium und Aluminium von Eisen wurde ausgearbeitet. In der ersten Stufe werden Eisen und Aluminium in einer Austauschsäule mit

einem Anionenaustauscher in Citratform aufgenommen, während Calcium in den Durchlauf geht. Danach wird Aluminium mit konzentrierter Salzsäure eluiert.

Die Methode wurde für Kalkanalysen verwendet.

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THE SEPARATION OF MOLYBDENUM VALENCIES BY PAPER CHROMATOGRAPHY

PART II[1]

by

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INTRODUCTION

Molybdenum has been recognized as an essential element of plant metabolism since the work of STEINBERG[2], and ARNON AND STOUT[3]. NICHOLAS AND NASON[4] have shown that the metal is an essential constituent of the enzyme nitrate reductase, and that a change in the valency of the metal takes place during the enzymic reduction of nitrate to nitrite. A method for separating the valency states of molybdenum was necessary in order to determine the valency changes undergone in the metabolism of micro-organisms and higher plants[5]. The separations were achieved using paper chromatography.

The quantitative separation of Mo^{VI} and Mo^{V} as thiocyanates has already been described[1]. The present work deals with the separation of hexa- and pentavalent molybdenum as oxine complexes, and of pentavalent and trivalent molybdenum.

EXPERIMENTAL

Separation of Mo^{VI} and Mo^{V} as oxinates

Mo^{VI} oxinate was prepared by mixing a solution of sodium molybdate dihydrate (1 g in 10 ml water), acidified with 2*N* hydrochloric acid (5 ml), and 8-hydroxyquinoline in ethanol (2 g in 20 ml). The mixture was heated and filtered through a Büchner funnel using Whatman No. 1 paper, and the bright yellow residue washed with water and ethanol and dried. The solid was recrystallized by allowing a hot filtered chloroform solution to stand overnight in the refrigerator, filtering off the deposited solid and washing it with ether. The complex was soluble to a small extent in acetone and chloroform, but almost insoluble in other organic solvents and water. Absorption maxima at 250 mμ and 370 mμ, and a minimum at 280 mμ were obtained with a chloroform solution as shown in Fig 1.

If excess of ethanolic oxine was added to a solution of sodium molybdate acidified with hydrochloric acid, and the mixture shaken with zinc dust, a dark purple colour was produced which on adding water and chloroform could be extracted into the latter.

A compound purporting to be Mo^{V} oxinate, which has not previously been reported, was obtained by (i) the addition of a solution of molybdenum pentachloride in 10*N* hydrochloric acid (0.5 g in 5 ml), which was treated with a little sodium amalgam to reduce traces of Mo^{VI}, to a solution of 8-hydroxyquinoline in ethanol (5 g in 50 ml) followed by 20 ml of water. The reddish-purple solution was allowed to stand for 5-10 minutes, filtered, (Whatman No. 41 paper) and poured into 500 ml of water. The mixture was heated to 50°-60°, filtered through a Büchner funnel (Whatman No. 1 paper), and the dark purple residue washed with cold water, ether and

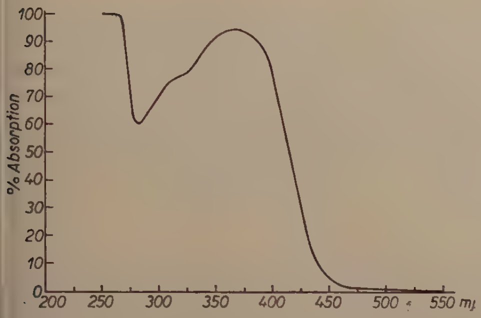

Fig. 1. Mo^{VI} oxine complex: spectrum in the U.V. and visible range.

then dried in an oven at 40°-50°. (ii) dissolving sodium molybdate dihydrate (1 g) and potassium thiocyanate (5 g) in water (20 ml), adding 10N hydrochloric acid (20 ml) and warming to 60°-70°. After allowing to stand for 10-15 minutes, the mixture was cooled and shaken with ether (150 ml). The upper ethereal layer was separated, filtered and then added to a solution of oxine in ether (5 g in 10 ml). The dark brown precipitate was filtered off, (Büchner funnel, Whatman No. 1 paper), and boiled with water for a few minutes. The purplish-black residue was filtered off, washed with cold water, ether and dried at 40°-50°. The same compound was formed if solutions of molybdenum pentachloride and oxine in carbon tetrachloride were mixed, and the resulting dark green precipitate was warmed with water for 5-10 min. Method (i) gave the purest product which contained molybdenum and oxine, and only a trace of chloride. The dark purple solid when dissolved in ethanol, acetone, ethyl acetate and chloroform gave reddish-purple solutions, but was almost insoluble in ether, carbon tetrachloride, and water. Absorption maxima at 243 mμ and 540 mμ, and a minimum at 480 mμ were obtained with ethanol solutions. (See Figs. 2 and 3.) The dark brown precipitate obtained in method (ii) contained molybdenum

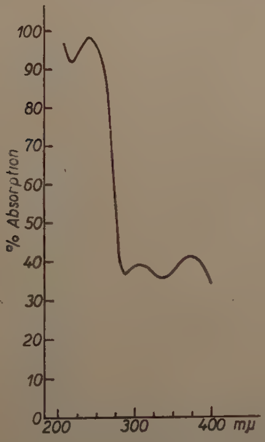

Fig. 2. Mo^{V} oxine complex: U.V. spectrum.

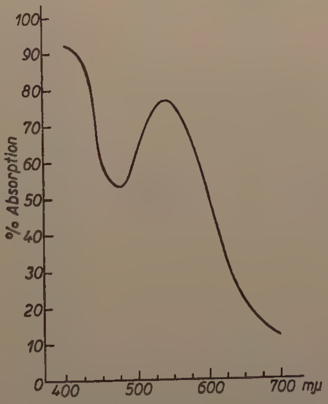

Fig. 3. Mo^{V} oxine complex: visible spectrum.

(3.6%), oxine, and thiocyanate, and the dark green precipitate from the carbon tetrachloride reaction contained molybdenum, oxine and chloride.

Analysis of the purple compound gave the following composition: Mo, 19.2% (spectrographic method); C, 50.3%; H, 3.1%; N, 6.25%.

When the complex was warmed with potassium thiocyanate and hydrochloric acid, it was decomposed yielding an orange solution of Mo^{V} thiocyanate. This afforded a colorimetric method for estimating the molybdenum content; 15-20 mg of the complex was heated with 10 ml of a 10% w/v solution of potassium thiocyanate in 2N hydrochloric acid and 2 ml of acetone. The orange-red solution was diluted to 100 ml with the thiocyanate reagent, and 5 ml portions extracted with known volumes of ethyl acetate. The colour of the extracts was measured on the Hilger "Spekker" as described previously[1]. A mean value of 22.0% was obtained. A "blank" determination using 15-20 mg of oxine was performed and could be neglected.

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It is suggested that the dark purple compound prepared by method (i) may be an "aquo" complex, while the brown and green products obtained by method (ii) are possibly "thiocyanato"- and "chloro"- compounds.

Separations between Mo^{VI} and Mo^{V} as oxinates were obtained on Whatman No. 1 paper strips by placing spots of a mixed chloroform solution on the starting line, allowing the chloroform to evaporate, and eluting with ethanol. R_F values were 0 for Mo^{VI} and 0.9-1.0 for Mo^{V}. The separation was, however, not quantitative as the recoveries of Mo^{V} in experiments on paper chromatograms and cellulose columns, were on average, about 7% below the theoretical values.

Separation of Mo^{V} and Mo^{III}

The preparation of a pure solution of Mo^{III} presented an initial problem. By the electrolysis of a solution of molybdenum trioxide in 10*N* hydrochloric acid at a current of 7-8 amp and using a platinum cathode[6], reduction of the molybdenum below the pentavalent state was not completely effected after about 6 hours operation. Molybdenum trichloride, prepared by heating the pentachloride in hydrogen, was found to be insoluble in all solvents except those which decompose it (*e.g.* nitric acid, sodium hydroxide). A satisfactory method for obtaining an efficient reduction of molybdenum trioxide below the penta-state consisted of adding zinc dust to a mixed solution of sodium molybdate (0.5 g in 5 ml water) and 10*N* hydrochloric acid (10 ml) until the solution ceased to give a red colour when portions were tested with potassium thiocyanate. The solution was then filtered (Whatman No. 41 paper) from excess of zinc dust, and freed from Mo^{V} and zinc as follows:

A cellulose column was prepared by drawing out one end of a piece of glass tubing 30 cm × 1.5 cm (internal diameter) into a jet into which was inserted a plug of glass wool to act as a porous retaining washer. The tube was filled with a suspension of Whatman powdered cellulose in water, and a compressed air supply was attached to the upper end. Water was thereby forced out of the tube, and the cellulose packed tightly and evenly into a column approximately 15 cm in length. 5 ml of the reduced molybdate solution was placed on the column and allowed to soak in; the inner wall of the tube above the cellulose was then wiped with filter paper. Elution was carried out using a solution of thiocyanic acid in ether until at least 15 minutes after the red band of Mo^{V} thiocyanate, together with zinc, had passed out of the column. The eluant was prepared by adding 10*N* hydrochloric acid (40 ml) to a solution of potassium thiocyanate (40 g in 40 ml water) and shaking the mixture with ether (150 ml). The upper ethereal layer was filtered and stored in a refrigerator. A further elution was then carried out using pure ether (to wash out thiocyanic acid) until the eluate was colourless. Distilled water was passed through the column and the orange eluate was collected and warmed to 40°-45° in a stream of carbon dioxide to expel ether. It was then diluted to 100 ml with distilled water.

The chloride solution thus prepared was found to be free of zinc, thiocyanic acid, and Mo^{V} and to possess strong reducing properties. In the presence of sulphanilamide (1% in *N* hydrochloric acid) nitrate was quantitatively reduced to nitrite. The estimation of the nitrite produced was performed colorimetrically using N-(1-naphthyl) ethylenediaminedihydrochloride (0.001% in water)[7].

The molybdenum content of the solution was estimated by mixing 0.5 ml with 10 ml of 10% potassium thiocyanate in 2*N* hydrochloric acid; 2-3 drops of hydrogen peroxide (10 vol.) were added and the red colour allowed to appear and begin to fade. A solution of stannous chloride was then added drop by drop until there was no further deepening of the restored red colour. The solution was extracted with 40-50 ml of ethyl acetate and the extract filtered and measured on the "Spekker" in the usual way.

The valency state of the zinc-reduced solution of Mo was determined as follows: To 1 ml of a solution of sodium molybdate, acidified with hydrochloric acid, and containing 12.5 mg Mo per ml, 5 ml of 10*N* hydrochloric acid and 2.5 ml of water was added. Zinc dust was then added until the solution was orange-brown and ceased to give a red colour when a spot was mixed with potassium thiocyanate on a white tile. When all the zinc had dissolved, the solution was diluted to 100 ml with distilled water. Portions were then mixed with 50 ml of 2*N* sulphuric acid and titrated with standard potassium permanganate solution.

45 ml of reduced molybdate solution ($\equiv$ 5625 μg Mo) required 3.5 ml $N/20$ $KMnO_4$.
(Calc. for $Mo^{III} \rightarrow Mo^{VI} + 3e$, 3.51 ml; for $Mo^{IV} \rightarrow Mo^{VI} + 2e$, 2.34 ml).

40 ml of reduced molybdate solution ($\equiv$ 5000 μg Mo) required 15.6 ml $N/100$ $KMnO_4$.
(Calc. for $Mo^{III} \rightarrow Mo^{VI} + 3e$, 15.62 ml; for $Mo^{IV} \rightarrow Mo^{VI} + 2e$, 10.4 ml).

The molybdenum therefore appears to be trivalent, which agrees with the results obtained by previous workers[6,8,9].

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Good qualitative separations between Mo^{III} and Mo^{V} were obtained on acid-washed Whatman No. 1 paper strips using the ether-thiocyanic acid eluant, R_F values being 0 for Mo^{III} and 0.8-0.9 for Mo^{V}. The separations could not be performed quantitatively owing to the oxidation of some of the Mo^{III} to Mo^{V} by thiocyanic acid in the presence of air. The R_F value for Mo^{VI} in this system was 0.8-0.9, but a separation between Mo^{VI} and Mo^{III} could not be performed as these valency states interacted in thiocyanate solution giving Mo^{V}.

When solutions containing trivalent molybdenum and potassium thiocyanate were mixed and shaken with ether, no molybdenum was extracted unless air or hydrogen peroxide was added, when red Mo^{V} thiocyanate passed into the ether. Similarly no molybdenum could be extracted by chloroform from mixed solutions of Mo^{III} in water, and oxine in ethanol unless air was admitted, when reddish purple Mo^{V} oxinate passed into the chloroform layer. These observations suggested that thiocyanate and oxine compounds of trivalent molybdenum, if they exist, are less stable than those of Mo^{V} and are not formed under these conditions. The lack of movement of Mo^{III} in the ether-thiocyanic acid system may be due to the adsorption of the chloride onto the cellulose, while the more covalent molybdenum pentathiocyanate dissolves in, and moves with the organic eluant.

ACKNOWLEDGEMENTS

The author's thanks are due to Dr. D. J. D. NICHOLAS for information concerning the chemical reduction of nitrate by Mo^{III}, to Miss ANN PAGET and Mr. DEREK CLIFFORD for undertaking the estimation of nitrogen in the Mo^{V} oxine complex, and to Dr. MITCHELL of the Macaulay Institute, Aberdeen, for the estimation of molybdenum in the complex by spectrographic analysis.

SUMMARY

The preparation of Mo^{VI} oxinate and a purported Mo^{V} oxine complex is described. The latter was analysed, and a number of its properties, including separation from the Mo^{VI} compound by paper chromatography, were studied.

The preparation of a solution containing trivalent molybdenum and the separation of this valency from the pentavalent state by chromatography upon cellulose is also described.

Suggestions as to the stability of thiocyanate and oxine compounds of Mo^{III} were made from the results of some extraction experiments performed upon trivalent molybdenum solutions.

RÉSUMÉ

La préparation de l'oxinate de molybdène^{VI} et d'un complexe molybdène^{V}-oxine est décrite. Ce dernier a été analysé; un certain nombre de ses propriétés ont été étudiées, comprenant sa séparation d'avec le composé du molybdène^{VI} par chromatographie. La préparation d'une solution renfermant le molybdène^{III} et la séparation du molybdène^{III} d'avec le molybdène^{V}, par chromatographie sur cellulose, sont décrites. Des hypothèses ont été faites au sujet de la stabilité des thiocyanate et oxinate de molybdène^{III}, à partir des résultats de quelques essais d'extraction effectués avec des solutions de molybdène^{III}.

ZUSAMMENFASSUNG

Die Darstellung von Molybdän^{VI}-Oxinat und von einem Molybdän^{V}-Oxin-Komplex wird beschrieben. Dieser Letztere wurde analysiert; eine gewisse Anzahl seiner Eigenschaften wurde untersucht, unter anderen seine Abtrennung von der Molybdän^{VI}-Verbindung mittels Papierchromatographie. Die Darstellung einer Lösung, welche Molybdän^{III} enthält und die Abtrennung des Molybdän^{III} vom Molybdän^{V} mittels Zellulosechromatographie sind beschrieben. Es wurden Hypothesen aufgestellt in Bezug auf die Stabilität des Molybdän^{III}-Thiocyanats und -Oxinats, ausgehend von Resultaten einiger Extraktionsversuche, welche mit Lösungen von Molybdän^{III} ausgeführt wurden.

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ANALYSIS OF MIXTURES OF THE CONDENSED PHOSPHATES BY ION-EXCHANGE CHROMATOGRAPHY

I. MIXTURES OF ORTHO-, PYRO-, TRI-, TETRA-, TRIMETA-, AND TETRAMETAPHOSPHATES AND GRAHAM'S SALT

by

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In previous papers from this laboratory, a theoretical discussion was given of the elution behavior of polyprotic acids[1], and a method was described for the analysis of mixtures of ortho-, pyro-, tri-, trimeta-, and tetrametaphosphates[2]. In this paper, a modification of the method is described by which complete analyses may be obtained of mixtures containing the five above-mentioned phosphates plus tetraphosphate and Graham's salt.

APPARATUS AND REAGENTS

Four columns were used. Each had an internal cross-sectional area of 3.8 sq.cm and was filled to 14 cm with resin AG 1-X8, 100 to 200 mesh. Each column was provided with a water jacket connected so that the resin beds in all columns could be heated simultaneously with one circulating pump. The AG resin was obtained from Bio-Rad Laboratories, 800 Delaware Street, Berkeley, California; it is Dowex 1-X8 that has been carefully sieved and washed with acids, bases, and complexing agents. The shipment received in this laboratory was found to give narrower elution graphs and hence better separations than the resin previously[1,2] used, Dowex 1-X10, 100 to 200 mesh.

The fraction collector, pH meter, spectrophotometer, and most of the reagents have been described[1,2].

The eluant designated as 0.250M potassium chloride of pH 9.00 was actually 0.240M with potassium chloride and 0.010M with ammonium chloride and contained sufficient ammonia to give a pH of 9.00. Similarly, a mixture of 0.490M potassium chloride, 0.010M ammonium chloride and ammonia is designated as 0.500M potassium chloride of pH 9.00.

Guanidinium tetraphosphate monohydrate was prepared by the method of QUIMBY[3] except that the quantity of formamide used was 20% greater than recommended by QUIMBY. The analysis of this product is given in Table 1.

The Graham's salt was prepared by TREITLER[4], who also found its number-average degree of polymerization to be 190.

ELUTION GRAPHS

The solid graph in the upper part of Fig. 1 presents a quantitative separation of ortho-, pyro-, tri-, tetrameta-, and trimetaphosphates by elution at a flow rate of 0.6 cm per minute with three different concentrations of potassium chloride, each buffered at a pH of 5.00. The dashed line of this same figure indicates the behavior of tetraphosphate under the same elution conditions. Although the two tetramers are clearly separated from other phosphates, it is obvious that these elution conditions will not effect their separation from each other.

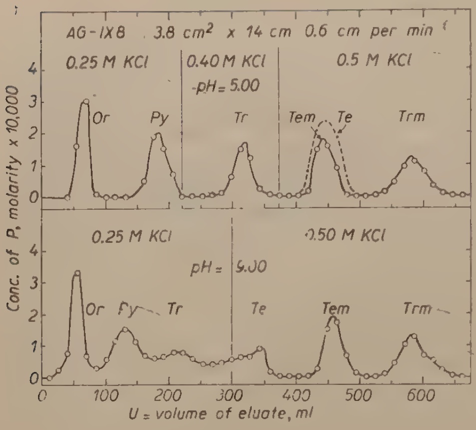

Fig. 1

The lower graph of Fig. 1 shows an elution at the same flow rate with two concentrations of potassium chloride at pH 9.00. The two cyclic phosphates are completely separated from each other and from the other phosphates under these conditions, but the ortho-, pyro-, tri-, and tetraphosphates overlap each other. Thus two elutions, one at pH 5.00 and one at pH 9.00, furnish all the data needed for the complete analysis of a mixture of the six compounds mentioned above.

If a sample containing Graham's salt is eluted at a pH of either 5.00 or 9.00 with these eluants, it remains absorbed on the upper part of the column even though several liters are passed through. However, treatment of the absorbed Graham's salt with hot 3.0*M* hydrochloric acid hydrolyzes it to lower polymers which are readily eluted from the column.

METHOD OF ANALYSIS

The sample should contain not more than 0.15 milligram atom of phosphorus in any one compound. Dissolve it in 5 ml of 0.250*M* potassium chloride buffered at pH 5.00. Add it cautiously to the resin column, previously equilibrated by the passage of 200 ml of this eluant. Drain the column at a flow rate of 0.2 cm per minute into a 250 ml graduated cylinder until the meniscus is within about 1 mm of the top of the resin. Wash the walls of the column above the resin bed with three 5-ml portions of the same 0.250*M* potassium chloride solution. After each addition of wash-solution, drain the liquid level to within 1 mm of the resin bed at a flow rate of 0.2 cm per minute.

Now elute with 220 ml of 0.250*M* potassium chloride, 150 ml of 0.400*M* potassium chloride, and 310 ml of 0.500*M* potassium chloride, each buffered at a pH of 5.00. Maintain a flow rate of 0.6 cm per minute or 2.3 ml per minute. Collect successive fractions of eluate of 110, 140, 140, 120, and 170 ml. These contain, respectively, the ortho-, pyro-, tri-, the mixture of tetra- and tetrameta-, and trimetaphosphate. Each fraction except the fourth contains only one species of phosphate.

Heat the column to 70 to 80° C by pumping hot water through the jacket. Pass 200 ml of 3.0*M* hydrochloric acid through the column at the same flow rate. Collect as the final fraction 200 ml of eluate.

Determine the phosphate content of each fraction by the depolymerization and photometric method previously described[1,2]. The last fraction must be evaporated to dryness and redissolved in water before the photometric method is applied.

Perform a similar elution simultaneously on a column previously equilibrated with 500 ml of 0.250*M* potassium chloride at pH 9.00. Use 300 ml of this eluant, 370 ml of 0.500*M* potassium chloride, and 200 ml of 3.0*M* hydrochloric acid as before. Collect fractions of eluate of 400, 120, 150, and 200 ml. These contain, respectively, the mixture of orthophosphate with the first three linear polymers, the tetrameta-, the trimetaphosphate and the depolymerized Graham's salt.

If calculation method A (see below) is to be applied, it is necessary to determine only the tetrametaphosphate in the second fraction, although the analyst may wish to determine also the trimetaphosphate in the third fraction and the depolymerized Graham's salt in the fourth fraction as checks on the elution at pH 5.00.

If means are not available for heating the columns, equally good results can be obtained in the following manner. Pass 50 ml of 3.0*M* hydrochloric acid through the column at room temperature. Let the column stand overnight in contact with the acid. Then pass an additional 175 ml of 3.0*M* hydrochloric acid through the column. In this case, the last fraction will have a volume of 225 ml.

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Calculations

If the phosphorus found in the second fraction of eluate of pH 9.00 is subtracted from the phosphorus found in the fourth fraction of the eluate of pH 5.00, the difference is the amount of phosphorus present in the sample as tetraphosphate. This is designated as Method A.

If the sum of the phosphorus found in the elution at pH 5.00 as ortho-, pyro-, and triphosphate is subtracted from the phosphorus found in the first fraction of the eluate of pH 9.00, the difference is the phosphorus present in the sample as tetraphosphate. This is designated as Method B.

It is assumed in the foregoing statements that exactly the same weights of sample were taken in both elutions. If this is not the case, the quantities of phosphate found in the elution at pH 9.00 should be proportionately corrected on the basis of the sample weight taken for the elution at pH 5.00.

RESULTS

In order to test the purity of the individual phosphates used in this investigation, samples of each of the seven phosphates were subjected to the foregoing analytical methods. The results are listed in Table I. Each entry is the mean of three determinations. The maximum value of the absolute mean deviation is 1.3%; and the average value, exclusive of those with 0.0 percentage, is 0.6%. All results except those for the guanidinium tetraphosphate and Graham's salt were calculated on a dry basis.

TABLE I

ANALYSIS OF INDIVIDUAL PHOSPHATES

Phosphate Taken	*Percent of total P present as*						
	Ortho	*Pyro*	*Tri*	*Tetra*	*Tetrameta*	*Trimeta*	*Graham's Salt*
K_2HPO_4	99.9	0.0	0.0	0.0	0.0	0.0	0.0
$Na_4P_2O_7$	3.6	95.7	1.7	0.0	0.0	0.0	0.0
$Na_5P_3O_{10}$	1.7	5.0	88.8	0.6	0.3	0.0	2.9
$(GuH)_6P_4O_{13}$	4.2	1.6	2.9	79.9	0.0	0.0	0.0
$Na_4P_4O_{12}$	1.2	0.5	1.5	1.6	95.2	0.6	0.0
$Na_3P_3O_9$	3.0	1.6	0.0	0.0	0.0	95.3	0.0
$(NaPO_3)n$	0.0	0.0	0.0	0.0	3.1	3.9	91.4

As a test of the accuracy of the method, mixtures containing known quantities of each of the phosphates were prepared and submitted to analysis. These results are shown in Table II. Each entry under the headings "Found" is the mean of two independant determinations. For hexaguanidinium tetraphosphate, two results are given — the first obtained by Method A, the second by Method B of the calculations. It is seen that results of very satisfactory accuracy are obtained by both methods of calculation.

TABLE II

ANALYSIS OF PHOSPHATE MIXTURES

Phosphate	*Mixture 1* *90.9 mg* *Taken* %	 *Found* %	*Mixture 2* *69.6 mg* *Taken* %	 *Found* %	*Mixture 3* *70.1 mg* *Taken* %	 *Found* %
K_2HPO_4	22.0	22.2	29.3	29.2	12.4	12.4
$Na_4P_2O_7$	14.5	14.4	7.8	7.9	20.0	19.9
$Na_5P_3O_{10}$	12.7	12.6	16.8	16.7	7.0	6.8
$(GuH)_6P_4O_{13}$	21.9	A 22.0 B 21.7	12.4	A 12.2 B 11.9	31.2	A 30.8 B 31.5
$Na_4P_4O_{12}$	9.9	10.0	14.9	14.7	9.1	9.1
$Na_3P_3O_9$	9.2	9.1	5.3	5.3	14.7	14.8
$(NaPO_3)_n$	9.8	9.7	13.5	13.5	5.6	5.5

DISCUSSION

If four elutions, two at each pH, are performed simultaneously, a duplicate analysis can be completed in 8 hours. The attention of the operator is required for much less than half of this time.

Recently, two papers have been published that report the analysis of mixtures of condensed phosphates by paper chromatography. GERRITSMA AND FREDERIKS[5] have determined ortho-, pyro-, tri-, and trimetaphosphates and Graham's salt in mixtures. WESTMAN AND CROWTHER[6,7] have used paper chromatography to determine phosphorus compounds up to nonaphosphate. The results for the lower members (including tetraphosphate) were accurate to ±0.8% of the total phosphorus. Results for penta-, hexa-, septa-, octa-, and nonaphosphate were precise to ± 2% of the total phosphorus. Molecules that contained more than nine phosphorus atoms were reported as "high polymers." Thus it is seen that paper chromatography has at present succeeded in isolating more members of the series of polyphosphates than ion-exchange chromatography. The latter technique, however, requires much less time and yields more accurate results.

HIGGINS AND BALDWIN[8] have used ion-exchange chromatography to analyse mixtures of orthophosphoric acid with its linear polymers as high as pentaphosphoric acid. They used unbuffered eluants. The duration of their elutions was 14 hours. The precision of their method seems to be about the same that as of the method described in this paper.

U. P. STRAUSS AND T. L. TREITLER of this laboratory are studying the kinetics of the depolymerization of Graham's salt in aqueous solution. In the course of this investigation, they analyse partially degraded Graham's salt by the method described in this paper. Anomalous results are obtained with samples of extensively depolymerized Graham's salt. It is believed that pentaphosphate is present in these extensively degraded samples and interferes in the analytical procedure by appearing with trimetaphosphate at pH 5.00 and with tetrametaphosphate at pH 9.00. Work is being continued to develop analytical methods for the analysis of phosphate mixtures containing pentaphosphate and higher polymers.

The theoretical principles of ion-exchange chromatography, previously discussed[1], were used to develop the methods of analysis described in this paper. Although the

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exchange constants and ionization constants of tetraphosphoric acid were not evaluated, the elution characteristics of this compound could be predicted with fair accuracy by extrapolation of the series, ortho-, pyro-, and triphosphoric acids.

It is well known that commercial ion-exchange resins differ slightly from batch to batch. Therefore, a different batch of Dowex 1-X8 may require slightly different elution conditions to yield quantitative separations such as those described in this paper.

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The authors are grateful to the Atomic Energy Commission of the United States for financial assistance in this work and to U. P. Strauss and T. L. Treitler for samples of Graham's salts, for determinations of the average molecular weight of these samples, and for general advice.

SUMMARY

When a mixture of condensed phosphates is eluted on a column of Dowex-1 with various concentrations of potassium chloride buffered at pH 5.00, appropriate fractions of the eluate contain (1) orthophosphate, (2) pyrophosphate, (3) triphosphate, (4) a mixture of tetra- and tetrametaphosphates, and (5) trimetaphosphate. A similar elution with eluants buffered at pH 9.00 yields eluate fractions containing (1) a mixture of ortho-, pyro-, tri-, and tetraphosphates, (2) tetrametaphosphate, and (3) trimetaphosphate. In both elutions, Graham's salt is retained on the column until it is treated with hydrochloric acid. Thus two elutions serve for the determination of the seven constituents.

RÉSUMÉ

Lorsqu'on rince un mélange de phosphates condensés, sur une colonne de Dowex-1, avec des solutions de chlorure de potassium, à diverses concentrations, à pH 5.00, on obtient les fractions d'éluat suivantes: (1) orthophosphate, (2) pyrophosphate, (3) triphosphate, (4) mélange de tétra- et tétramétaphosphates et (5) trimétaphosphate. Une élution similaire avec des solutions éluantes à pH 9.00 donne des fractions d'éluat contenant: (1) mélange d'ortho-, de pyro-, de tri- et tétraphosphates, (2) tétramétaphosphate, et (3) trimétaphosphate. Dans ces deux élutions, le sel de Graham reste dans la colonne; il est traité ensuite par l'acide chlorhydrique. Deux élutions suffisent donc pour le dosage des sept constituants.

ZUSAMMENFASSUNG

Man eluiert ein Gemisch von kondensierten Phosphaten aus einer Säule von Dowex-1 mit Kaliumchloridlösungen von verschiedenen Konzentrationen bei pH 5.00. Geeignete Teile des Eluats enthalten dann (1) Orthophosphat, (2) Pyrophosphat, (3) Triphosphat, (4) eine Mischung von Tetra- und Tetrametaphosphaten, und (5) Trimetaphosphat. Eine ähnliche Elution bei pH 9.00 gibt Teile des Eluats, die (1) eine Mischung von Ortho-, Pyro-, Tri-, und Tetraphosphaten, (2) Tetrametaphosphat, und (3) Trimetaphosphat enthalten. In beiden Elutionen bleibt das Graham'sche Salz am Harz bis man es mit Salzsäure behandelt. Man erzielt also eine Bestimmung aller sieben Phosphatarten durch zwei Elutionen.

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APPLICATION OF VAPOUR PHASE CHROMATOGRAPHY IN THE GAS-ANALYTICAL FIELD

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INTRODUCTION

Chromatography in its various forms has found an extremely wide application in laboratory science and in industry.

The analysis of mixtures of components in the gas or vapour phase represents one of the most recent applications in chromatography. The techniques employed for this purpose — which are generally known collectively as vapour phase chromatography — have rapidly become of great importance in the analytical field owing to their rapidity, selectivity and ease of execution with automatic recording equipment.

Vapour phase chromatographical methods may be subdivided into two groups:
(a) those employing a solid adsorbing agent (gas-solid chromatography);
(b) those using a liquid agent for partition (gas-liquid chromatography).

Gas-solid chromatography may again be carried out in two forms. The methods first employed were based on separation by displacement. The gaseous mixture is adsorbed onto activated charcoal or silica gel in a column and subsequently desorbed selectively by a gradual increase in temperature[10,20], or else it is displaced by a vapour that is more powerfully adsorbed[3,9].

In the second method of gas-solid chromatography (gas-solid elution chromatography) the adsorbed components are eluted by means of an inert stripper gas. The latest developments in this field have been described by JANAK[13], PATTON[18] and RAY[19]. The great forces with which the components are bound to solid adsorbents allow the low molecular weight gases, such as hydrogen, nitrogen, rare gases, methane, ethane and propane, to be separated. For the separation of the high molecular weight compounds, however, the strong adsorption is a drawback. A corresponding increase in column temperature to weaken these forces of adsorption gives rise to the risk of chemical reactions. Complete desorption may be realized by displacement with a vapour of greater adsorbability, but each analysis requires a fresh charge in the column[4,8]. Furthermore, the possibilities of the gas-solid elution technique are limited by the small number of suitable adsorbents, as well as by the considerable influence of their quality and of the pretreatment they have undergone on the sharpness of separation.

Gas-liquid partition chromatography proves to be much more attractive for the analysis of hydrocarbon gases. In 1952 MARTIN and co-workers[11,12] gave a detailed description of the separation of volatile compounds according to this principle.

The procedure is as follows. The chromatographic column is charged with a non-volatile absorption liquid (the stationary phase) on an inert solid carrier and the volatile mixture to be separated is eluted from the column with the aid of an inert stripper gas. The components of the mixture pass through the column at a velocity proportional to their respective Henry-coefficients and their concentrations in the stripper gas can be measured at the outlet of the column. If the non-volatile absorption liquid is stable, the contents of the column may be used for an unlimited number of runs.

Obviously, the fact that there is a wide range of suitable absorption liquids of greatly varying selective properties renders this technique much more flexible than gas-solid chromatography; the liquid phase can be selected in accordance with the separation problem in question. Several of these absorption liquids are discussed in detail by KEULEMANS and co-workers[14].

Applications of this analytical separation technique to gas mixtures have been described by RAY[19] and BRADFORD[1].

The present paper discusses a few aspects of the separation of hydrocarbon gases (C_1–C_5) and the quantitative determination of the components in more detail.

EQUIPMENT

Fig. 1 shows the principle of the apparatus employed for the form of analysis to be described first. It is provided with a device for measuring thermal conductivity. A gas sample of known volume is introduced by the stripper gas into the column, where it is subjected to separation; the changes in concentration of each component in the gas leaving the column are recorded by means of thermal conductivity measurement. Figs. 2-5 give a few examples of the type of chromatogram obtained in this way.

SEPARATION

The quantitative analysis of a mixture in the first place requires an effective separation of the components. The theory of gas-liquid partition chromatography which was developed by MARTIN[12] and others gives some guiding principles that are of importance for the separation, but owing to the large number of factors playing a part in the process it is not yet possible to predict the optimum conditions for each problem.

The main factors of importance for separation are:

(a) factors determining the Henry-coefficient:
the nature of the absorption liquid and the column temperature;

(b) the other operational variables:
the dimensions of the column, the size of sample, the type of carrier, and the velocity of the stripper gas.

(a) The nature of the absorption liquid and the temperature determine the relative volatility of the components to be separated in the column. The retention volumes of the components, or the retention times at a given velocity of the stripper gas, are inversely proportional to the respective Henry-coefficients of these components.

An effective analytical separation can be realized if the ratio of the retention volumes of two components is higher than 1.10.

Theoretically a low temperature promotes the separation, but fortunately this influence is not a critical one and mixtures with a boiling range of 50 or even 100° C can be analysed at a single column temperature. By a suitable choice of the other conditions (*e.g.* the column length), hydrocarbon gas mixtures both in the methane-ethane range and in the butane-pentane range can be separated at a temperature of +30° C. Thus, the apparatus retains its simple and flexible character.

The choice of the liquid phase is determined by the nature of the compounds to be separated. If a non-polar liquid (*e.g.* "liquid paraffin") is used, the hydrocarbons are separated virtually according to boiling point. Hence this type of immobile phase gives an easy separation of the saturated hydrocarbon gases C_1 to C_5, but not, say, of mixture of 1,3-butadiene (b.pt. —4.4° C), *iso*-butene (—6.9° C) and 1-butene (—6.3° C).

The solubility of olefins in polar liquids is considerably greater than that of the corresponding paraffins. If the liquid phase consists of dimethyl sulpholane (b.pt. 280° C), for instance, propene (b.pt. —48° C) and propane (b.pt. —42° C) leave the column in reverse order, the retention time of the propane being shorter than that of propene.

Dimethyl sulpholane cannot, however, effect the complete separation of *iso*-butene and 1-butene*. Dimethyl formamide (b.pt. 155° C) can be used for this purpose (see Fig. 5), but has the drawback that at 0° C the vapour tension is still 0.8 mm, so that the separating power of the column gradually decreases owing to loss of the immobile phase. For quantitative work this is a disadvantage.

BRADFORD[1] has pointed out that it is possible to separate olefins by using a glycolic solution of $AgNO_3$ as the liquid phase. This may be explained by the fact that these olefins form unstable complexes[6] with $AgNO_3$. The unsaturated C_4 hydrocarbons are separated in the order: *trans*-2-butene (b.pt. +0.9° C), *iso*-butene (—6.9° C), *cis*-2-butene (+3.7° C), 1-butene (—6.3° C), 1,3-butadiene (—4.4° C). The butanes do not form complexes and pass through the column very quickly without being separated. As glycols are very hygroscopic the stripper gas and the samples must be perfectly dry in order to keep the separating power of the column constant. It was found that for this reason a saturated solution of $AgNO_3$ in benzyl cyanide is preferable to a similar solution in glycol.

An important tool for the separation of complex gas mixtures is a system of two columns with different liquid phases. By placing these in series and choosing suitable lengths it is often possible to separate one component from those which would cause interference if each of the columns were used separately. This point will be further discussed when dealing with the examples.

(b) If the concentrations of the components in the stripper gas are plotted against time (volume of stripper gas), a chromatogram as shown in Figs. 2-5 is obtained. The ratios of the retention times of the components are exclusively determined by the nature of the liquid phase and the temperature of the column. If, however, substances differing little in volatility have to be separated, the peak widths are very important for quantitative analysis. It is mainly the diffusion phenomena occurring in the column, which determine the width of a peak.

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* FREDERICKS AND BROOKS[17], however, succeeded in getting sufficient separation for analytical use, but only by using columns of 15 m length (private communication).

For the vapour-liquid equilibrium to be established rapidly the liquid must be deposited on the inert solid carrier in a very thin layer. Most investigators have used Celite 545 (grain size 20–40 μ) as carrier with about 30%w of liquid. It has been found that a smaller quantity of liquid (15-25%w) often improves the separation. At the same time, this has the advantage of reducing the time required for analysis; the retention volumes are directly proportional to the quantity of liquid phase in a column. The viscosity of the liquid phase also plays a rôle in equilibration. The choice is limited, however, as the requirements of polarity and low volatility must also be satisfied.

The velocity of the gas is not a very critical factor, although at high and low velocities the peaks tend to become wider on account of both back diffusion and incomplete equilibration. For 6 mm diameter columns with Celite as the carrier these "critical" values are approximately $\frac{1}{2}$ and 5 l/h respectively. At gas velocities higher than 3 l/h, however, columns charged with Celite are unsuitable, as their resistance is high (*ca.* 0.4 atm per 2 m of length at 3 l/h). Therefore a search was instituted for a carrier material with a lower resistance, which would make it possible to use longer columns for difficult separations without the need of more time for the analysis.

Certain screen fractions of ground insulating bricks[15] (*e.g.* Sterchamol*) as carriers give complete satisfaction. The resistance of this material at a grain size of 50-80 mesh (0.2-0.3 mm) is a third of that of Celite, but the separations effected are practically equivalent. At larger grain sizes (30-50 mesh = 0.3-0.6 mm) the efficiency of separation is slightly reduced. Sterchamol need not be subjected to a special pretreatment, except for removal of dust by suspension in water and drying at 150° C. The liquid phase can be deposited by diluting it with a volatile solvent (say 1 to 5), mixing it with the carrier and evaporating the solvent with continuous stirring. Besides the low resistance, the fact that the method of filling the columns is simple and shows better reproducibility, provides an important advantage of Sterchamol over Celite. As this new carrier material permits the use of columns with a length of 6 m, the separation of CH_4, C_2H_2, C_2H_4 and C_2H_6 no longer presents any difficulties.

In actual practice use is made of column sections of 2 m length, which are interconnected as and when required. Copper columns, after having been filled, can be coiled in order to save space.

Experiments carried out with columns of different diameters varying from 4 to 14 mm have shown that the separation efficiency is independent of the column diameter so long as the size of the sample is varied in proportion and the linear gas velocity remains the same. Within these limits no disturbing radial diffusion apparently occurs. Hence the column diameter can be adapted to the measuring system used for the determination of the components.

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* Sterchamol is a proprietary brand of refractory brick.

For a separation in a given column and with otherwise identical experimental conditions, there is an advantage in reducing the size of the samples. In quantitative analysis the lower limit is determined by the sensitivity of the measuring system. In columns with a diameter of 6 mm we use gas samples of 1-20 ml (NTP), according to the desired separation or the accuracy with which traces have to be determined.

QUANTITATIVE ANALYSIS

Two methods have been used for detecting and measuring the components separated in the column:

1. continuous measurement of the concentration of the components in the stripper gas leaving the column, on the basis of differences in thermal conductivity (indirect determination);
2. Determination of the absolute quantity of each component by volume or pressure measurement, after removal of the stripper gas (direct determination).

Re 1.

Various methods, based on the measurement of a physical quantity, can be used for an indirect determination. In their publications GRIFFITH[8] and HAMMAR[9] give many references on the subject.

Of all these methods we chose thermal conductivity, as it combines sensitivity with comparative simplicity, and no difficulties are encountered in recording.

The thermal conductivity cell used in this laboratory is of the Bureau of Mines type, as described by PALMER AND WEAVER[17]. It consists of a copper block pierced by two parallel channels 10 cm in length and 3 mm in diameter, in which platinum wires 0.02 mm in diameter are stretched. The gas mixture flows through one channel, the stripper gas used as reference through the other. The platinum wires are connected to a source of electricity and form two arms of a Wheatstone bridge. The out-of-balance voltage of the bridge, caused by the different resistance of the two wires due to differences in heat conduction, is recorded by means of a 0-2½ mV Brown pen recorder. The cell is placed in the same air thermostat as the sample inlet system and the columns and is maintained at a temperature of 30 ± 0.2° C.

The changes in concentration of the components in the stripper gas leaving the column are thus measured continuously, so as to yield a chromatogram of a differential type as shown in Figs. 2-5.

The area of a peak is proportional to the quantity of the component in question if the gas velocity is constant and the deflection of the thermal conductivity device is directly proportional to the concentration of that component in the stripper gas. This frequently is the case for concentration up to 10%.

Instead of measuring the actual peak area it is usually sufficient to determine it approximately, for instance by multiplying the peak height by the width halfway up[5], or by drawing the tangents to the peak and multiplying the width at the base thus obtained by the height. As the various gases differ greatly in thermal conductivity the relation between peak area and quantity of component must be determined with the aid of pure substances or synthetic gas mixtures.

Peak heights are easier to determine than peak areas, but the measurement of peak heights requires a greater constancy of separating conditions. A change, *e.g.* of temperature or column charge, results in a different *shape* of the peak, the peak *area* remaining the same. Quantitative analysis based on peak height measurements is consequently only used for the determination of low concentrations of a component (< 10%) in products whose main composition varies little; this restriction is also necessary owing to the fact that the shape of the peak for a given component is not entirely independent of the other components in the mixture analysed.

The latter influence makes itself felt chiefly in the first part of the column and might be explained as follows. As the heaviest component dissolves in the stationary phase, the concentration of lighter components in the gas increase, with the result that the concentration at which the latter dissolve is also higher. Consequently the peak height of the light component increases, the base becoming narrower. The influence of light components on the peak shape of the heaviest components is small. Tables I and II record the results of a series of measurements on mixtures of various compositions.

TABLE I

INFLUENCE OF COMPOSITION OF SAMPLE ON PEAK HEIGHT OF A COMPONENT

Column : length 200 cm; diam. 7 mm;
liquid phase: C_{19}-paraffins on Sterchamol
Stripper gas : nitrogen, 2 l/h
Size of sample : 10 ml

Percentage of component in sample	*Peak height for 1% of component*										
	C_2H_6 in				*C_3H_6 in*	*C_3H_8 in*			*n-C_4H_{10} in*		
	N_2	*C_3H_6*	*C_3H_8*	*C_4H_{10}*	*C_2H_6*	*N_2*	*C_2H_6*	*C_4H_{10}*	*N_2*	*C_2H_6*	*C_3H_8*
5	3.25	—	4.64	4.28	—	5.84	5.75	6.27	4.22	4.30	4.16
10	3.23	4.15	4.18	3.88	5.66	5.48	5.36	5.73	3.98	4.00	3.91
50	2.24	—	2.51	2.20	—	3.11	3.01	3.46	2.61	2.72	2.61
90	1.71	1.69	1.70	1.71	2.73	2.48	2.49	2.48	2.04	2.01	2.05
95	1.66	—	1.66	1.67	—	2.41	2.42	2.43	1.98	2.00	1.98
100	1.64	—	1.64	1.64	—	2.36	2.36	2.36	1.98	1.98	1.98

TABLE II

INFLUENCE OF COMPOSITION OF SAMPLE ON PEAK AREA OF A COMPONENT

Percentage of component in sample	*Peak area for 1% of component*										
	C_2H_6 in				*C_3H_6 in*	*C_3H_8 in*			*n-C_4H_{10} in*		
	N_2	*C_3H_6*	*C_3H_8*	*C_4H_{10}*	*C_2H_6*	*N_2*	*C_2H_6*	*C_4H_{10}*	*N_2*	*C_2H_6*	*C_3H_8*
5	19.2	—	19.5	20.2	—	53.7	54.8	56.3	89.8	90.1	90.0
10	19.7	20.0	20.1	19.5	56.6	53.8	54.7	56.2	87.8	89.8	89.7
50	19.9	—	20.3	20.9	—	56.0	54.5	56.2	89.0	89.2	89.4
90	20.4	20.1	19.6	19.2	59.5	55.5	55.9	54.5	89.5	89.7	89.7
95	20.3	—	20.0	20.6	—	56.0	55.1	56.4	87.7	88.5	89.7
100	20.5	—	20.5	20.5	—	55.9	53.8	56.7	90.0	90.0	90.5
Mean	20.0	20.0	20.0	20.1	58.0	55.2	54.8	56.0	89.0	89.6	89.8

The fact that the components do not affect each other over the whole length of the column is apparent from the following experiments, which were carried out in columns of various lengths.

TABLE III

INFLUENCE OF COLUMN LENGTH ON THE SHAPE OF THE PEAK OF A COMPONENT IN TWO DIFFERENT MIXTURES

Length of column, cm	*Peak height for 1 % of component*			*Peak area for 1 % of component*	
	10% C_2H_6 in			*10% C_2H_6 in*	
	N_2	*C_3H_8*	*Difference*	*N_2*	*C_3H_8*
200	3.23	4.18	29%	19.7	20.1
400	2.48	2.85	15%	20.3	19.9
600	2.04	2.15	5%	19.8	19.6

The percentage differences between peak heights for C_2H_6 in mixtures with N_2 or with C_3H_8 are 29% in the 2 m column and only 5% in the 6 m column.

The peak areas as determined by the method of tangents are practically independent of the length of the column and of the other components, as is apparent from Tables II and III.

If the peak height is taken as a measure of the content of a component, calibration should be carried out with synthetic mixtures whose composition is about the same as that of the gases to be analysed.

Area measurement is suitable for analysing mixtures whose composition is in sufficiently known. In this case calibration is simpler because, unlike peak height, the area increases proportionally with the content.

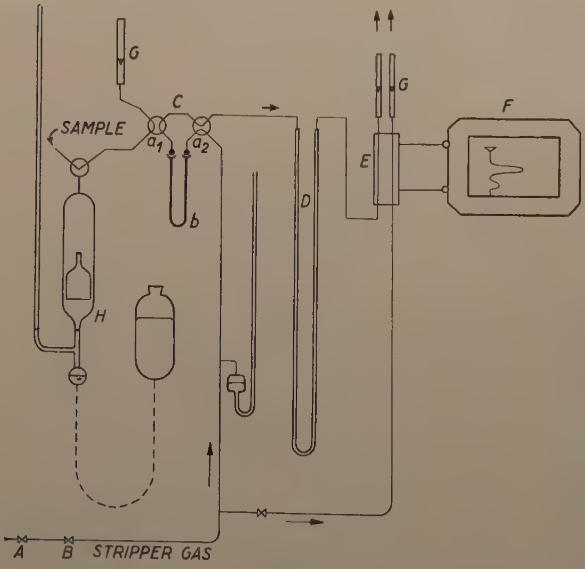


Fig. 1. Gas analysis apparatus with thermal conductivity recording.

A. Technical reducing valve
B. Precision reducing valve
C. Sample inlet system
a_1 a_2 Four-way cocks
b. Sample tube
D. Separating column
E. Thermal conductivity cell
F. mV Recorder
G. Rotameters
H. System for preparing calibration mixtures

For the accuracy of the method it is of paramount importance that gas samples of constant volume should be introduced into the column in a reproducible way. The best results were obtained with the device shown in Fig. 1, in which a given volume of gas is confined between two four-way cocks and, on opening one of these, is entrained by the stripper gas. By measuring the gas sample at barometric pressure and keeping the pressure in the thermal conductivity cell equal to atmospheric, variations in barometric pressure are automatically corrected. The stop cocks must be lubricated with a hydrocarbon-insoluble lubricant. A mixture of starch, mannitol and glycerol[2] is excellent; products such as vaseline and silicones are entirely unsuitable.

A value of general validity for the accuracy of this form of gas analysis cannot be given, as it is dependent on many factors differing for each type of gas mixture.

With the apparatus described, the method of peak height measurement yields more accurate results than that of area measurement if a stable stationary phase, for instance, a non-volatile liquid paraffin, is used. In this case calibrations for peak heights are very nearly constant and components that are completely separated from the remainder can be determined to within about 2% of the actual percentage, with a lower limit of about 0.05% absolute, *i.e.* the content is determined as 50.0 ± 1.0% mol, 10.0 ± 0.2% mol, or 1.00 ± 0.05% mol.

Area measurements have to be employed when the calibration cannot be carried out on mixtures of corresponding composition, or when the stationary phase is not sufficiently stable.

Peak area measurements, however, show a greater spread than peak height measurements, because measuring the length of the base introduces additional errors. The deviations in analytical results are at least twice as large as those based on peak height measurements.

The maximum accuracy is ultimately determined by the accuracy with which the calibration mixtures can be composed.

The sensitivity of the thermal conductivity measurement can, moreover, be influenced by the nature of the stripper gas. The difference in conductivity, for instance, between the C_2 hydrocarbons and N_2 is only small, so that CO_2 is preferable as stripper gas. On the other hand, CO_2 is not very suitable for the analysis of C_4 and C_5 hydrocarbons. By using the correct stripper gas it is possible to detect contents of 0.1% of each of the C_1-C_5 hydrocarbons in gas samples of 5-10 ml.

TABLE IV

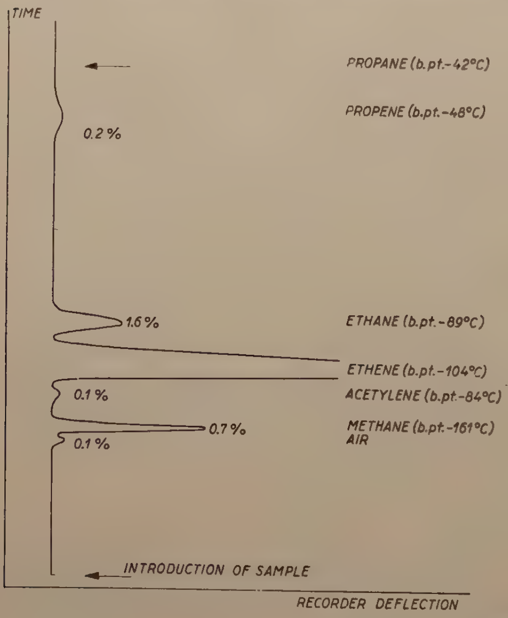
ANALYSES OF GAS MIXTURES WITH THE AID OF VARIOUS STATIONARY LIQUIDS

Sample	*Ethene*	*Propane-Propene*			*Butane-Butene*
Figure	2	3	4		5
Size of sample, ml	5	5	2		5
Chrom. column:					
length, m	6	2	1 +	5	4
diameter, mm	6	6	6	6	6
temperature, °C	+30	+30	+30	+30	0
Stationary liquid	liquid paraffin	liquid paraffin	liquid paraffin	dimethyl sulpholane	dimethyl formamide
Conc. of st. liq. on support, %w	30	15	15	25	25
stripper gas	CO_2, 3 l/h	N_2, 3 l/h	N_2, 3 l/h		N_2, 3 l/h
Time of analysis, minutes	12	8	20		20

The advantages of the thermal conductivity method are that:

1. the required measuring and recording equipment is fairly simple, and
2. after use the apparatus is immediately ready for the next analysis.

The method has the drawback that each thermal conductivity cell must be calibrated for all components under the conditions (temperature, gas velocity) at which it will be used. Examples of the type of gas mixtures that can be analysed with the aid of thermal conductivity measurements are given in Table IV and Figs. 2-5.



Liquid paraffin (transformer oil, b.pt. *ca.* 300° C) is a suitable liquid phase for the determination of the contaminations in ethene (Fig. 2). As the solubility of the low molecular weight components at 30° C is only small, 30% of liquid paraffin is deposited on the carrier (Sterchamol, 50-80 mesh) and a 6-metre column is used.

Fig. 2. Analysis of technical ethene with liquid paraffin as the stationary liquid.

Liquid paraffin is also very suitable for the determination of high and low boiling components in propane and propene (Fig. 3). The components are separated according to boiling point. If the product contains large quantities of propane and propene they are separated only to a very slight extent.

The determination of C_3 and C_5 hydrocarbons in a butane-butene product can be done in the same way. The analysis takes about 20 minutes (up to and including 2-methyl-2-butene) if the stripper gas has a flow rate of 5 l/h.

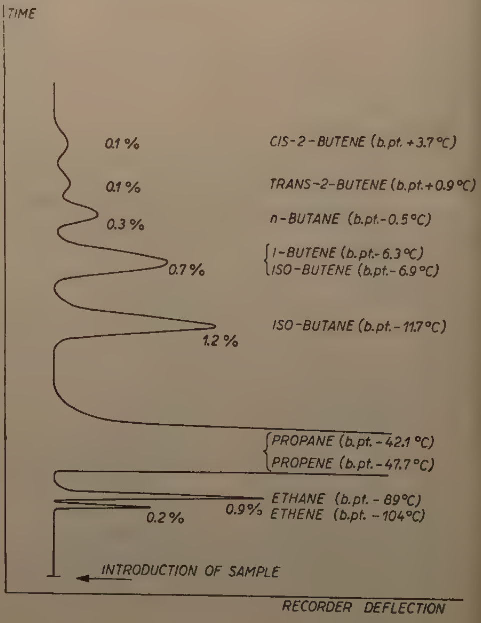


Fig. 3. Determination of low and high-boiling components in technical propane.

Propane and propene can be separated with dimethyl sulpholane, but *iso*-butane has the same retention time as propene and thus causes interference. If, however, a column containing dimethyl sulpholane is combined with one containing liquid paraffin, the latter effects a separation according to boiling point and the determination of propene is no longer disturbed by the *iso*-butane (Fig. 4).

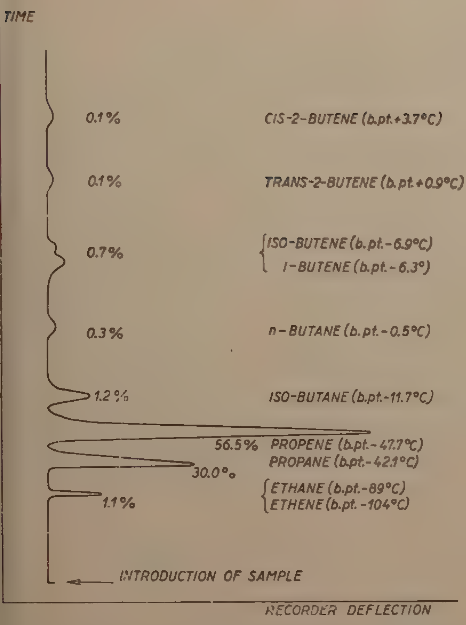


Fig. 4. Analysis of a propane-propene mixture with dimethyl sulpholane as the stationary liquid.

Iso-butene and 1-butene cannot be separated with liquid paraffin and only partially with dimethyl sulpholane. By the use of a strongly polar liquid, such as dimethyl formamide (Fig. 5), the separation of the components can be achieved; 1-butene leaves the column before *iso*-butene, notwithstanding the fact that its boiling point is somewhat higher.

Re 2.

Quantitative analysis by direct measurement of the quantity of a component after removal of the stripper gas has the advantage that no calibration with gas mixtures of known composition is required.

Even if a complete chromatographic separation is not effected, a direct measure of the total quantity of each fraction is obtained, which is not the case if the thermal conductivity method is employed. The temperature of the column and the rate of stripping need not be constant; they can, if necessary, be changed during analysis so as to obtain optimum separations in a minimum of time.

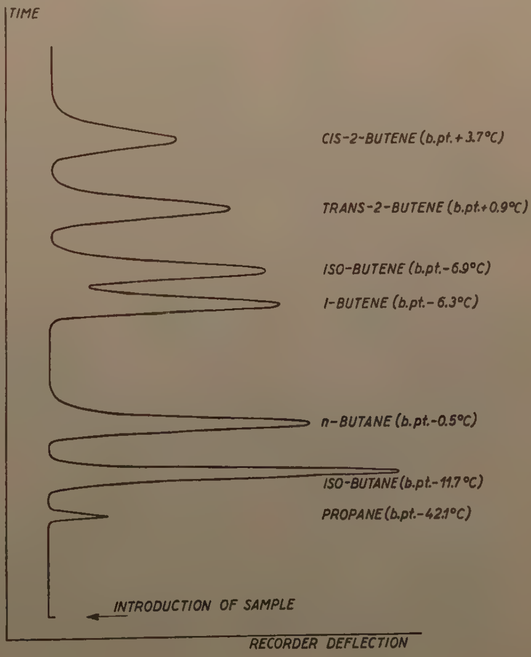


Fig. 5. Analysis of a butane-butene mixture, with dimethyl formamide as the stationary liquid.

Carbon dioxide, a gas that can be absorbed in alkaline solutions without undergoing disturbing reactions with hydrocarbons, is practically the only suitable stripper gas for this method.

The quantities of gas can be determined in two ways, *viz.* by measuring either the gas volumes at constant pressure or the increments in pressure occurring in a vessel of constant volume. The simplest method is volume measurement in a nitrometer filled with a KOH solution, a method which JANAK[13] and others have followed in gas-solid chromatography. For the determination of low molecular weight gases (permanent gases and hydrocarbons up to propane) this method of measurement gives excellent results. The analysis of gas mixtures containing higher molecular weight compounds is affected by inaccuracies due to the fact that, for instance, butenes dissolve in the relatively large quantity of absorption liquid. CO_2 absorption in a separate small scrubber under reduced pressure improves the accuracy and makes it possible also to determine the components condensing at normal pressure. As, however, volume measurement cannot be combined with automatic recording in a simple way it has been replaced by pressure measurement.

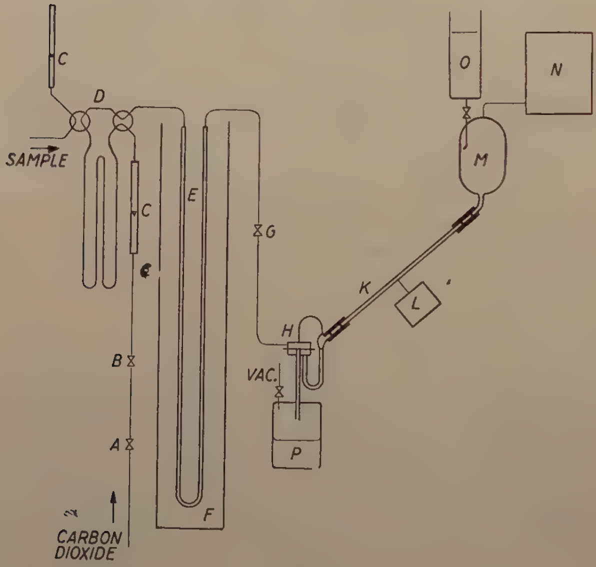


Fig. 6. Gas analysis apparatus with pressure recording

A. Technical reducing valve
B. Precision reducing valve
C. Rotameters
D. Sample inlet system
E. Separating column
F. Heating bath
G. Release valve
H. Level controller
K. CO_2 scrubber
L. Vibrator
M. Receiving vessel
N. Recording manometer
O. KOH-Solution
P. Spent caustic

Fig. 6 gives the principle of the apparatus developed for this method of measurement. After absorption of the CO_2 the components or fractions separated in the column are collected in an evacuated vessel and the increments in the pressure in this vessel are electrically recorded.

The manometer is an electromagnetic precision meter of the type described by KINKEL[16]. Over the range of 0-300 mm Hg the linearity is better than 0.1% of the full measuring range.

The absorption liquid (KOH, 50%w) flows to the absorber through the receiver and is removed through a level controller which functions independently of the gas pressure in the absorber. The requirements to be met by the absorber are that (a) complete absorption of the CO_2 is effected with a minimum quantity of absorbent, (b) no measurable back pressure occurs, and (c) its volume is small with respect to that of the receiver.

Good results have been obtained with a stainless steel tube of 50 cm length and 5 mm diameter, which is kept in vibration by an electromagnetic vibrator. The tube contains a loosely wound coil to prevent the KOH solution from flowing off too rapidly. At a pressure of 80 mm Hg a CO_2 stream of 6 l/h (atm) is still quantitatively absorbed, notwithstanding the fact that in this case the gas, on entering the absorber, has a linear velocity of *ca.* 80 cm/sec. The KOH solution, which flows at a rate of 2 ml/min, reaches a temperature of *ca.* 60° C on the outlet side, so that its solvent power for the hydrocarbon gases is nil.

The separation of 100 ml of gas mixture is effected in a column of 6 m length and 12 mm diameter. In this way a pressure rise of 0.1 atm is obtained in a 1-litre receiver. On account of the vapour tension of the KOH solution and with a view to proper functioning of the absorber, the initial pressure cannot be chosen lower than 0.1 atm; consequently, the final pressure is *ca.* 0.2 atm.abs. At this pressure the percentage of C_5 and C_6 hydrocarbons in the gas mixtures, which are usually low, are still easily determined and no trouble is caused by condensation or deviation from the ideal gas laws.

The pressure at the end of the column is adjusted with a release valve and is independent of the changes in pressure in the receiver. The velocity of the stripper gas is controlled by means of the gas pressure at the inlet of the column.

The possibilities offered by the apparatus have not yet all been ascertained, but it seems likely that the components and fractions separated can be determined with an accuracy of at least ±0.3% on the total sample.

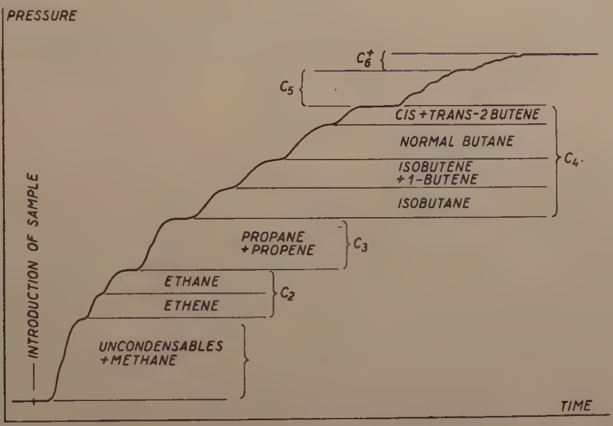


Fig. 7. Analysis of a full-range cracked gas.

Fig. 7 gives an example of the analysis of a gas obtained by catalytic cracking of a petroleum fraction. In order to effect a satisfactory separation of the light components and yet complete the analysis in an hour's time use was made of a long column (6 m), the temperature of which, during the analysis, was gradually increased from +20° C to +80° C. In this case the stationary liquid phase was liquid paraffin.

As is shown by this example the method is particularly suitable for the analysis of gas mixtures consisting of a large number of components comprising a wide boiling range. For the analysis of simple mixtures or the accurate determination of low concentrations (< 1%) the thermal conductivity method is, however, preferable.

On the strength of the experience gained with vapour phase chromatography in the past few years, it appears justified to expect that this method will come to occupy an important place among the many other physical methods for the analysis of hydrocarbon gases and other volatile products, such as low-temperature distillation, infrared, ultraviolet and mass spectrometry.

On account of its relatively low cost, its simplicity of operation and the rapid interpretation of the results, chromatography is an ideal method for production control.

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ACKNOWLEDGEMENT

The author is indebted to the management of the Koninklijke/Shell-Laboratorium, Amsterdam for permission to publish these results, and wishes to thank Miss TH. C. J. M. WENTHOLT and Messrs. J. D. KOMMER AND J. C. BANSBERG for their co-operation in the experimental work and Mr. A. SCHURINGA for the development of the electromagnetic manometer.

SUMMARY

Of the various types of gas chromatography developed in the past few years gas-liquid partition chromatography has been found to be the best method for the analysis of hydrocarbon gases.

By a suitable choice of the liquid phase and the other conditions it is possible to separate each individual hydrocarbon in the C_1-C_5 range from the other components. The influence of size of column nature of carrier material, concentration of liquid phase on carrier, and gas velocity, has been discussed.

For the quantitative determination of the components two methods were used, *viz.*:

(a) Continuous measurement of the thermal conductivity of the gas mixture leaving the column. This method is preferred for the analysis of gas mixtures consisting of a limited number of components and for the determination of a single component in a complex mixture.

(b) Measurement of the pressure increments obtained by collecting the components in an evacuated vessel after the CO_2 stripper gas has been removed by absorption in a caustic solution. This method is particularly suitable for the analysis of gas mixtures consisting of many components with widely different boiling points.

RÉSUMÉ

Parmi les différents types de chromatographie en phase gazeuse, mis au point ces dernières années, la chromatographie de partition gaz-liquide s'est trouvée être le meilleur moyen pour l'analyse d'hydrocarbures gazeux.

Par un choix judicieux de la phase liquide et des autres conditions, il est possible d'isoler chaque hydrocarbure dans la série C_1-C_5. L'influence des dimensions de la colonne, de la nature du support, du pourcentage de la phase liquide sur le support, et de la vitesse des gaz a été examinée.

Pour la détermination quantitative des composants, deux méthodes ont été employées, à savoir:

(a) La mesure en continu de la conductibilité thermique du mélange gazeux sortant de la colonne. On préfère cette méthode pour l'analyse de mélanges gazeux constitués d'un nombre limité de composants et pour la détermination d'un seul composant dans un mélange complexe.

(b) La mesure de l'accroissement de pression, obtenu en recueillant les composants dans un récipient évacué, après l'élimination du CO_2 par absorption dans une solution de potasse caustique. Cette méthode convient particulièrement bien à l'analyse de mélanges constitués de nombreux composants présentant une grande différence de points d'ébullition.

ZUSAMMENFASSUNG

Es hat sich herausgestellt, dass von den verschiedenen in letzter Zeit entwickelten Arten der Gaschromatographie die Gas-Flüssigkeits-Verteilungschromatographie das beste Hilfsmittel für die Analyse von Kohlenwasserstoffgasen ist.

Bei geeigneter Wahl der flüssigen Phase und der übrigen Bedingungen ist es möglich, jeden einzelnen Kohlenwasserstoff der C_1-C_5 -Reihe von den anderen zu trennen. Der Einfluss der Dimensionen der Kolonne, der Art des Trägermaterials, der Konzentration der flüssigen Phase auf dem Träger und der Gasgeschwindigkeit wurde bestimmt.

Zur quantitativen Bestimmung der Komponenten kamen zwei Methoden zur Anwendung, und zwar:

(a) Ununterbrochene Messung der Wärmeleitfähigkeit des aus der Kolonne tretenden Gasgemisches. Diese Methode hat den Vorzug für die Analyse von Gasgemischen mit einer beschränkten Anzahl Komponenten und für die Bestimmung einer einzigen Komponente in einem Mehrkomponentengemisch.

(b) Messung der Drucksteigerungen, die durch Sammlung der Komponenten in einem evakuierten Gefäss, nachdem das CO_2-Gas durch Absorption in Lauge entfernt worden ist, bewirkt werden. Diese Methode eignet sich besonders zur Analyse von Gasgemischen, die aus vielen Komponenten eines sehr weiten Siedebereiches bestehen.

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THE USE OF OXALYLDIHYDRAZIDE IN A NEW REACTION FOR THE SPECTROPHOTOMETRIC MICRODETERMINATION OF COPPER

by

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Some years ago NILSSON[1] noticed that an intensive blue-violet to violet color was obtained if a very weak solution of a copper salt was mixed with ammonium hydroxide, oxalyldihydrazide, and a large excess of formaldehyde or acetaldehyde. NILSSON suggested that the color obtained in this new reaction might be more intensive and less sensitive to changes in the pH value of the solution than that obtained in a reaction with bis-cyclohexanone-oxalyldihydrazone previously described[2,3]. Some qualitative data about the new reaction will be published by NILSSON in the near future.

With these reasons in mind an investigation was started to find a highly sensitive, selective and specific spectrophotometric method for the determination of microamounts of copper (5 to 50 μg).

I. *Oxalyldihydrazide and formaldehyde*

Solutions

1. *Standard copper solution.* A solution containing 6.0 mg of Cu^{+2} per litre.
2. *Oxalyldihydrazide.* A saturated solution. Excess reagent is dissolved in hot water. After cooling the clear solution is decanted from the crystals.
3. *Ammonium hydroxide.* A concentrated solution.
4. *Formaldehyde.* A 40% solution.

The preparation of the oxalyldihydrazide is very simple[4]. Equimolecular amounts of a diester of oxalic acid and of hydrazine hydrate, each dissolved in five volumes of alcohol, are mixed. In less than an hour a nearly quantitative yield is obtained. The product is washed with a little alcohol and recrystallized from boiling water.

NILSSON suggested[1] that the order of mixing the solutions might have a pronounced effect upon the color intensity. The optimal proportions of the reagent solutions were ascertained in a few trial runs, and then a series of experiments was carried out where the order of addition of the four reagents was varied in the twenty four possible ways: 10 ml portions of each solution were added successively to a 50 ml volumetric flask which was then filled to the mark with distilled water. The absorbancy was measured at 565 mμ in a Beckman spectrophotometer model B. A statistical analysis of the values obtained showed that the formaldehyde should be added later than all the other reagents.

The order of addition of the remaining solutions was unimportant, and it was choosen to add them in the order: copper solution, ammonium hydroxide, and oxalyldihydrazide.

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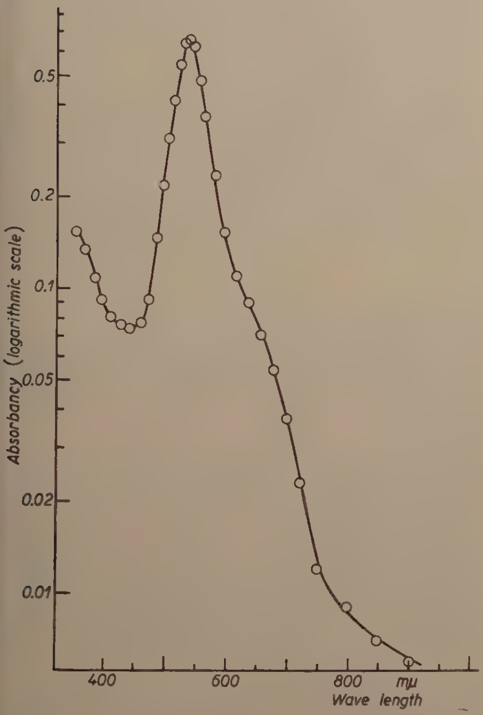

Fig. 1. Absorbancy curve for the violet color obtained in mixing a copper solution with ammonium hydroxide, oxalyldihydrazide and acetaldehyde.

It was found that the most intensive color is obtained when the pH value of the solution is in the range 5 to 10. Above pH 10 the color intensity diminishes rapidly with increased alkalinity. In the range 3 to 5 the color intensity seems to depend on the kind of acid used for buffering the solution. Phosphoric acid seems to decrease the color intensity much more than do acetic and hydrochloric acid.

II. Oxalyldihydrazide and acetaldehyde

Solutions

1 — 3. Same as before.
5. *Acetaldehyde.* A 40% solution.

According to NILSSON's findings[1], the color obtained with acetaldehyde instead of formaldehyde has a violet tinge. The absorbancy was measured as a function of the wavelength on a solution prepared by mixing:

10 ml of a copper solution (60 μg Cu^{+2})
5 ml of conc. ammonium hydroxide
4 ml of a saturated oxalyldihydrazide solution
10 ml of a 40% acetaldehyde solution

and diluting to 50 ml in a volumetric flask.

The curve found is shown in Fig. 1. The maximum, which is situated at about 542 mμ, is much more pronounced and much higher than with formaldehyde and it is also much more pronounced than in the reaction with bis-cyclohexanone-oxalyldihydrazone and gives a value for the molar absorbancy index of about $\varepsilon = 29{,}500$ or log $\varepsilon = 4.47$. This is most certainly the highest value hitherto found for any copper reagent.

In the same way a series of experiments was made where the concentration of copper was varied. The absorbancy is plotted versus copper concentration in Fig. 2. It is obvious that Beer's law is followed very closely.

The color obtained is very stable. It increases during the first few minutes but after about 30 minutes it remains stable for at least several hours.

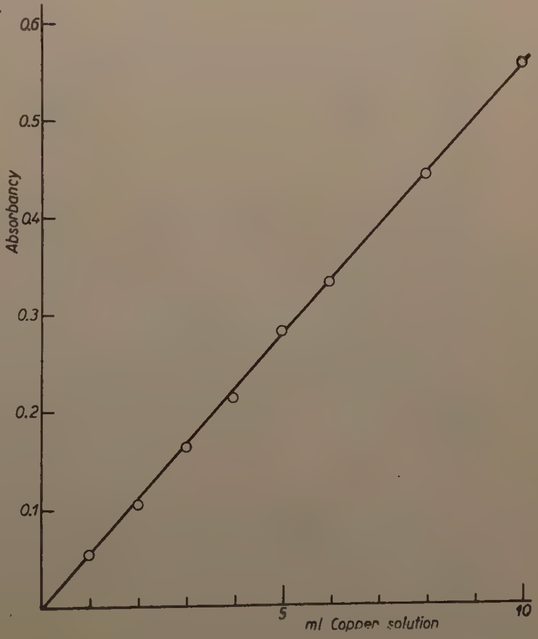

Fig. 2. Calibration curve for the violet color showing that Beer's law is followed.

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Some experiments showed that the presence of reasonable amounts of hydrochloric, nitric, and perchloric acid or of sodium sulfate had no influence on the absorbancy.

As reagent grade acetaldehyde could only be supplied in anhydrous form and was therefore fairly expensive, a regular grade and also a purified product[5] were tested. Fortunately no difference in absorbancy or other properties of the colored solutions could be detected. The small amounts of impurities encountered in the regular grade aldehyde therefore do not seem to have any influence on the reaction or the stability of the color.

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The author wants to thank civ.-ing. G. NILSSON, Chemical Laboratory, Department of Building Technique, Royal Institute of Technology, Stockholm, for valuable discussions and for many suggestions during this investigation and also for a supply of highly purified acetaldehyde.

SUMMARY

A new reaction for the spectrophotometric microdetermination of copper is described. To a strongly ammoniacal solution containing traces of copper is added a saturated solution of oxalyldihydrazide and formaldehyde or preferably acetaldehyde. A blue-violet to violet color of unusually high intensity is obtained. The absorbancy maximum is situated at about 542 mμ and the molar absorbancy index has a value of about 29,500 ($\log \varepsilon = 4.47$). This value is most certainly the highest hitherto known for any copper reagent.

The order of addition of the reagents is of great importance. The aldehyde should definitely be added last. The purity of the aldehyde does not seem to be of any great importance for the intensity or stability of the color.

RÉSUMÉ

Une nouvelle réaction pour le microdosage spectrophotométrique du cuivre est décrite. A une solution fortement ammoniacale renfermant des traces de cuivre, on ajoute une solution saturée d'oxalyldihydrazide et de formaldéhyde, ou mieux d'acétaldéhyde. Une coloration bleu violet à violette d'une extraordinaire intensité est obtenue. L'absorption maximum se trouve à environ 542 mμ et le coefficient d'extinction moléculaire est d'environ 29,500 ($\log \varepsilon = 4.47$). Cette valeur est très certainement la plus élevée parmi celles des réactifs du cuivre connus actuellement. L'ordre d'addition des réactifs est très important. L'aldéhyde doit absolument être introduit le dernier. La pureté de l'aldéhyde ne semble pas jouer un grand rôle sur l'intensité ou la stabilité de la coloration.

ZUSAMMENFASSUNG

Eine neue Reaktion für die spektrophotometrische Mikrobestimmung von Kupfer wird beschrieben. Eine stark ammoniakalische, kupferhaltige Lösung wird mit einer gesättigten Lösung von Oxalyldihydrazid und mit Formaldehyd oder — noch besser — Acetaldehyd versetzt. Dabei entsteht eine blauviolette bzw. violette Farbe von ausserordentlich hoher Intensität. Das Absorptionsmaximum liegt bei ungefähr 542 mμ und der molare Absorptionskoeffizient hat einen Wert von ungefähr 29,500 ($\log \varepsilon = 4.47$). Dieser Wert ist wahrscheinlich der grösste, der bisher für Kupferverbindungen gefunden worden ist.

Die Reihenfolge, in der die Reagenzien zugesetzt werden, ist von entscheidender Bedeutung für die Farbstärke. Die Aldehydlösung muss unbedingt zuletzt zugesetzt werden. Die Reinheit des Aldehyds scheint von untergeordneter Bedeutung für Stärke und Stabilität der Farbe zu sein.

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COLORIMETRIC DETERMINATION OF TRACES OF TIN WITH DITHIOL

by

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The work described here was done to provide a color method for determining traces of tin in natural materials. Available photometric procedures are intended for amounts of tin greater than about 40 γ, and are not applicable without modification to such samples.

At the present time an entirely satisfactory colorimetric reagent for tin is lacking. Dithiol appears to be the best of a number of reagents that have been used for the determination of relatively small amounts of tin. Both on the basis of sensitivity and selectivity it is superior to 8-hydroxyquinoline, cacotheline, diethyldithiocarbamate and hematoxylin. Although tin is usually separated from other elements by distillation procedures before determination, traces of heavy metals may be introduced in the subsequent treatment of the distillate and can cause trouble if the colorimetric reagent is not selective and minimal amounts of tin are to be determined. Dithiol reacts with many metals in acidic solution but the reaction products do not have the characteristic bright red color of tin(II) dithiolate.

When tin dithiolate is extracted by suitable organic solvents the color of the extract is pale yellow and not red, and immiscible solvent extraction does not appear to have any advantage. A colloidal dispersion of tin dithiolate must therefore be used for photometry or colorimetry[1,2,3]. Such methods have certain disadvantages. However, the present work has shown that a fairly satisfactory determination of 3 to 50 γ or more of tin can be made photometrically in this way (error usually less than 10% with more than 20 γ). Below 3 γ, a visual comparison method enables tin to be determined to ± 0.5 γ. The concentration sensitivity of the present procedure with a 1 g sample is 0.5 p.p.m., which is at least as good as the best arc spectrographic methods in use today.

The procedure described below was worked out with silicate rocks and meteorites particularly in mind, but it should be quite generally applicable. The separation of tin is made in the standard way, by distillation from hydrobromic acid solution.

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Apparatus

The distilling flask is a modification of SCHERRER's[4]. By means of a 34/45 standard taper joint the upper portion carrying the separatory funnel, thermometer well, and outlet tube is fitted to a 200 ml round-bottomed flask. The condenser (30 cm in length) is connected to the side arm by a 12/30 standard taper joint.

Solutions

Water, redistilled in Pyrex.

Nitric acid, concentrated, distilled in Pyrex.

Hydrochloric acid, 6*N*. Dilute the concentrated acid with an equal volume of water and distil.

Hydrobromic acid, 48%. Distil in Pyrex, rejecting the first and last 1/5.

Sulfuric acid. Volatilize possible traces of tin by adding dropwise a mixture of 15 ml of 6*N* hydrochloric acid with 2 ml of hydrobromic acid to 100 ml of 1 : 1 sulfuric acid and 10 ml of 6*N* hydrochloric acid at 150-160° C. Then add 10 ml of 6*N* hydrochloric acid drop by drop at the same temperature. Finally boil the sulfuric acid for another 10 minutes, cool, and dilute to 100 ml with water. Great care must be taken to remove all hydrobromic acid.

Dithiol, 0.1 g in 50 ml of 1% sodium hydroxide. Add 0.3-0.5 ml of thioglycolic acid as stabilizer. The solution may be used for a week if kept in a refrigerator.

Thioglycolic acid, at least 80% strength. Avoid the use of old products.

Santomerse S (Monsanto Chem. Co.). (1) Dilute 10 ml of the 30% solution to 40 ml with water (1 : 3). (2) Dilute 2 ml of the 30% solution to 40 ml with water (1 : 19).

Selenious acid, 1 mg Se per ml. Treat 100 mg of selenium with 1 to 2 ml of concentrated nitric acid and evaporate to dryness. Add 1 ml of concentrated hydrochloric acid and again evaporate to dryness. Dissolve the residue in 10 ml of concentrated hydrochloric acid and dilute to 100 ml with water.

Sulfurous acid. Prepare fresh daily by saturating water with sulfur dioxide.

Standard tin solutions. Dissolve 0.100 g of tin in 10 ml of concentrated hydrochloric acid and dilute to 100 ml with water after adding 0.5 ml of thioglycolic acid (1.00 mg Sn per ml). This solution may be kept for 2 weeks. (1) 100 γ Sn per ml solution. Dilute 10 ml of the stock solution to 100 ml with 1 : 19 hydrochloric acid. This solution can be kept for 2 days. (2) 10 γ Sn per ml solution (1 : 19 hydrochloric acid). Prepare fresh daily.

PROCEDURE

General directions for distillation and determination of tin

Transfer the sample solution to the distilling flask with 25 ml of 1 : 1 sulfuric acid, 5 g of KH_2PO_4 (or 3 ml of 85% phosphoric acid)*, 20 ml of 6*N* hydrochloric acid and 1 g of hydrazine sulfate.

Dip the end of the condenser into 30 ml of water in a 150 or 250 ml beaker. Pass a slow stream of carbon dioxide through the solution and boil gently. When the temperature has reached 160° C, introduce 6*N* hydrochloric acid dropwise at a rate of 1 drop every 4 seconds while maintaining the temperature at 155 to 165° C. When about 20 ml of hydrochloric acid has been added, remove the burner and beaker after washing the stem of the condenser with water. Discard the distillate and washings (contain arsenic).

Place a 100 ml beaker containing 15 ml of cold water under the condenser. Add a mixture of 15 ml of 6*N* hydrochloric acid and 7 ml of hydrobromic acid drop by drop while maintaining the temperature at 145 to 160° C and passing in carbon dioxide. This requires 15 to 20 minutes. Remove the burner, lower the beaker, and wash down the stem of the condenser.

To the distillate add 0.50 ml of 1 : 2 sulfuric acid and 5 ml of concentrated nitric acid and heat covered on a steam bath or a low temperature hot plate. When vigorous reaction has ceased, remove the cover glass, evaporate to a small volume, and finally fume for 3 to 5 minutes.

If the amount of tin is expected to exceed 3 γ, apply the photometric method: Add 4 ml of water and transfer the solution to a 10-ml volumetric flask and make up to about 7 ml with water. Add 1 drop of thioglycolic acid and mix. Add 0.05 ml of 1 : 19 Santomerse S, swirl gently, add 0.50 ml of dithiol solution and mix. Heat at 50 ± 5° C in a water bath for 5 ± 1 minutes. Then add 0.5 ml of 1 : 3 Santomerse S and mix. Cool, dilute to the mark with water, and mix. Measure the absorbance at 530 mμ without undue delay. Establish the standard curve by taking 0, 5, 10, 30, and 60 γ of tin, adding 0.50 ml of 1 : 2 sulfuric acid, and proceeding as described above. To obtain the reagent blank, run 5.0 γ of tin through the whole procedure and deduct 5.0 γ from the amount of tin found.

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* Potassium phosphate is preferred because of its lower tin content, but when the lowest possible blank is not required, phosphoric acid can be used, and has the advantage that it has no tendency to cause bumping.

When tin is less than about 3 γ use the visual comparison method: Add 2 ml of water to the sulfuric acid residue, transfer the solution to a 15-ml porcelain crucible, and wash the beaker with 1-ml portions of water. Evaporate to a drop by fuming. If the solution shows a brown color due to the presence of organic matter, add 0.1 g of ammonium persulfate and fume for a few minutes. Cool, add 0.25 ml of water, 1 drop of 1 : 5 thioglycolic acid (prepared immediately before use) and 1 drop of dithiol solution and mix. Heat on the steam bath for 3 minutes. Cool and compare the pink color with standards obtained by taking, *e.g.*, 0, 0.5, 1.0, 2.0, and 3.0 γ Sn, adding 0.50 ml of 1 : 2 sulfuric acid, fuming to a drop, and treating in the same way as the unknown.

Silicate rocks. The following directions are for silicate samples completely decomposable by hydrofluoric acid. Add 5 ml of 1 : 1 sulfuric acid, 0.5 to 1 ml of concentrated nitric acid, and 10 ml of hydrofluoric acid to 1.0 g of 100-mesh rock powder in a platinum dish and evaporate to strong fumes of sulfuric acid. Cool, add 1 ml of 1 : 1 sulfuric acid and 1-2 ml of water, and again evaporate to strong fumes. Transfer the residue with 25 ml of 1 : 1 sulfuric acid, 5 g of KH_2PO_4, 1 g of hydrazine sulfate and 10 ml of 6*N* hydrochloric acid to the distilling flask, and continue as in the general procedure above (usually by the visual method).

If cassiterite or other minerals not decomposed by hydrofluoric acid may be present, add to the residue from the hydrofluoric acid treatment 10 ml of 6*N* hydrochloric acid and 20 ml of water. Heat to near the boiling point and keep at this temperature until almost complete solution has been obtained. Filter through a medium-textured paper and wash with 2*N* hydrochloric acid and finally with water. Catch the filtrate and washings in the distilling flask.

Ignite the paper in a nickel crucible at a low temperature. Fuse the residue gently with 0.5 g of sodium hydroxide, and keep at dull redness for 30 minutes. Cool, and dissolve the melt in 8 ml of water. Transfer the solution to a beaker and carefully add 10 ml of 6*N* hydrochloric acid. Heat on a low-temperature hot plate for a few minutes and filter off the insoluble matter on a small medium-textured paper and wash the residue with 2*N* hydrochloric acid. Catch the filtrate and washings in the same distilling flask or carry out the distillation separately. If the tin content has been found to be relatively high (*e.g.* > 20 p.p.m.), fuse the residue again with sodium hydroxide and treat as described above. If much cassiterite is present, the preceding treatment may not recover all the tin. See DISCUSSION.

Iron (steel, iron meteorites). Dissolve 0.5 g of sample (1-100 p.p.m. Sn) in 7 ml of 1 : 1 sulfuric acid and 10 ml of 1 : 1 nitric acid. Evaporate and fume for a few minutes. Transfer the residue with 25 ml of 1 : 1 sulfuric acid, 5 g KH_2PO_4 (or 3 ml of 85% phosphoric acid), and 20 ml of 6*N* hydrochloric acid to the distilling flask containing 1 g of hydrazine sulfate. Carry out the distillation as described above. If the tin content of sample is likely to be less than 6 p.p.m. Sn use the visual method described above.

*Sulfides.** Treat 1.0 g of sample (0.5-50 p.p.m. Sn) with 10 ml of fuming nitric acid in a 100-ml beaker. Heat gently at first. When vigorous reaction has ceased, evaporate to a volume of 1 to 2 ml. Cool, add 7 ml of 1 : 1 sulfuric acid, and evaporate to strong fumes. Transfer the residue with 25 ml of 1 : 1 sulfuric acid, 5 g of KH_2PO_4 or 3 ml of 85% phosphoric acid, and 20 ml of 6*N* hydrochloric acid to the distilling flask containing 1 g of hydrazine sulfate. Carry out the distillation and determination of tin as described above (visual method for less than 3 p.p.m. Sn).

If selenium is likely to be present (*e.g.*, pyrite) treat the distillate as follows. After evaporation and fuming for 3 to 5 minutes, cool, add 4 ml of 6*N* hydrochloric acid and 0.1 ml of selenious acid (0.1 mg Se) and heat on a low temperature hot plate for about 5 minutes. Cool to room temperature, add 2 ml of saturated sulfurous acid and 0.2 g of hydroxylamine hydrochloride. Heat at 90° C for 1/2 to 1 hour. Collect the precipitate in a small porcelain filter crucible and wash with 1 : 99 hydrochloric acid, catching the filtrate and washings in a small beaker. Evaporate to fumes of sulfuric acid. Cool, add 2 ml of water, filter through a filter crucible, and wash with water. Catch the filtrate and washings in a 10-ml volumetric flask or a crucible depending on the expected amount of tin. Then continue as in the general procedure above.

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* This procedure is not intended for galena, the lead sulfate from which might retain tin. This point has not been tested.

DISCUSSION

Photometric and colorimetric determination of tin.

All the photometric procedures utilize a protective colloid to disperse stannous dithiolate. We have followed FARNSWORTH AND PEKOLA[3] in using Santomerse S for this purpose, but have introduced a number of changes.

With hydrochloric acid for acidification, a concentration of 0.4 to 0.6N is the most suitable, with sulfuric acid, a concentration of 0.4 to 0.8N. If the acidity is too high, Santomerse S is precipitated. If too little Santomerse S is present when dithiol is added, it is difficult to obtain a clear solution, even if more dispersing agent is added later. On the other hand, if its concentration is initially too high, color development is hindered. Thus 10 γ of tin will not give a color when 0.1 ml of 1 : 3 (v/v) Santomerse S is added. We have found that the most satisfactory procedure is to develop the color in the presence of a small amount of the dispersing agent and then to add more to stabilize the suspension.

Heating is required for rapid, full color development, when less than 20-30 γ tin is present in 10 ml. Heating at 100° with these amounts of tin causes decoloration after about a minute. This fading does not take place if the temperature is reduced to 50°. For more than about 30 γ of tin, color development at room temperature is satisfactory.

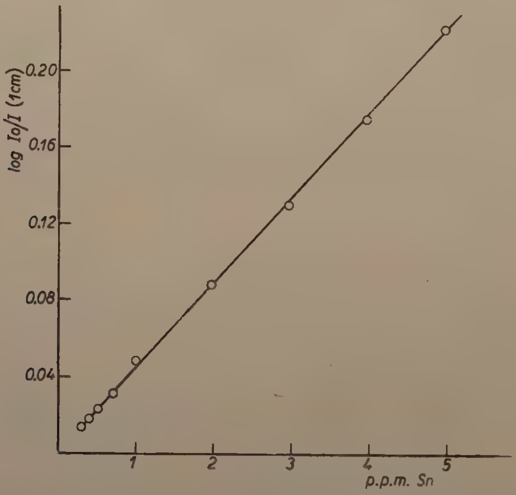

Fig. 1. Absorbance-concentration curve for determination of tin with dithiol (Leitz-Rouy photometer, 535 mμ filter). No color is produced below ∼0.3 p.p.m. Sn in solution.

Under the conditions recommended, absorbance is proportional to tin concentration in the range 0.25 to 6 p.p.m. or higher (Fig. 1). Below 0.25 p.p.m. Sn no color is produced. A number of factors may contribute to this: solubility of tin dithiolate, formation of supersaturated solutions, and inhibition of nucleation and particle growth by the dispersing agent. Therefore the photometric method fails when the tin concentration is less than 2.5 γ in 10 ml of final solution. To determine smaller

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amounts of tin it is necessary to reduce the volume of solution. This is conveniently done by using porcelain crucibles, developing the color in a volume of a few tenths of a milliliter without using a dispersing agent, and visually comparing the color with standards obtained similarly. As little as 0.5 γ of tin can be detected in this way. This procedure is simpler than collecting the tin precipitate on a disk of filter paper and comparing with similar standards (as done by SCHWAIBOLD *et al.*[10], and JANTSCH *et al.*[11]) and sufficiently accurate for small amounts of tin.

TABLE I

INTERFERENCE OF SOME IONS (DIRECT TEST)

Addition, γ	*Sn taken, γ*	*Sn found, γ*	*Remarks*
50 As	0	0.5, <0.5	
50 As	20.0	20.0, 20.0	100 γ As interferes (ppt.)
10 Sb	0	<0.5, <0.5	
10 Sb	20.0	20.5, 21.0	50 γ Sb interferes
5 Bi	0	2	5 γ Bi interferes
5 Bi	20.0	22.5	
10 Bi	0	3	
10 Bi	20.0	24	
90 Ge	0	<0.5, 0.0	
90 Ge	20.0	21.0, 19.0	
5 Mo	0	5	Mo interferes seriously
5 Mo	20	24.5	
10 Mo	0	7	
10 Mo	20.0	28	
50 Hg	0	0	1000 γ Hg gives ppt.
50 Hg	20.0	20.5	
10 Se	0	<0.5	50 γ Se gives white ppt. or turbidity
10 Se	20.0	20.5	
10 Te	0	<0.5	50 γ Te interferes (brown color)
10 Te	20	19.5	

TABLE II

SUMMARY OF CONDITIONS OF TIN BROMIDE DISTILLATION

*Volume ratio** *HBr/HCl*	*Temperature °C*	*Amount of tin*	*Author*
HBr only	220	0.25—2.5 mg	LAW[5]
6	180—185	10—200 mg	MOGERMAN[6]
2	137—147	0.04—0.8 mg	FARNSWORTH AND PEKOLA[3]
1/3	140	∿10 mg	SCHERRER[7]
1/3	130—140	Milligram quantities	KLINGER *et al.*[8]
1/3	135—145	—	BILTZ AND BILTZ[9]
1/3	130—140	Microgram quantities	SCHWAIBOLD *et al.*[10]
1/3	—	Microgram quantities	JANTSCH *et al.*[11]

* Of the concentrated acids. Sulfuric acid present in all to raise distillation temperature.

The effect of a few elements, particularly some that can be volatilized in distillation procedures, on the direct determination of tin was tested (Table I). Less than 50 γ of arsenic, germanium, and mercury or $\sim$ 10 γ of antimony, selenium and tellurium do not interfere, so that the separation of these elements need not be sharp. Molybdenum (green color) interferes seriously in very small amounts, and bismuth (reddish-brown color) almost as much.

TABLE III

BROMIDE DISTILLATION OF TIN

*Acid mixture**	*Temperature* °C	*Time min*	*Sn taken* γ	*Sn found* γ
14 ml HBr + 7 ml HCl	131—38	16	30	18
14 ml HBr + 7 ml HCl	131—38	25	30	18**
14 ml HBr + 7 ml HCl	147—60	25	30	28
10 ml HBr + 5 ml HCl	147—60	18	23	20
7 ml HBr + 7 ml HCl	150—60	18	20	16
7 ml HBr + 3.5 ml HCl	147—60	15	30	23
10 ml HBr + 10 ml HCl	150—60	25	30	30
7 ml HBr + 14 ml HCl	155—60	20	30	32
5 ml HBr + 15 ml HCl	140—50	25	23	20
5 ml HBr + 15 ml HCl	150—55	25	30	30

* HBr sp. gr. *ca.* 1.38, HCl 1.19; 30 mg of Fe(III) to oxidize Sn(II).
** Another 21 ml portion of HBr + HCl distilled at 147—57° yielded 16 γ Sn.

Separation of tin

The familiar hydrobromic-hydrochloric acid distillation is used. The conditions of distillation employed by earlier workers are summarized in Table II. From previous results and those of a few experiments carried out here (Table III) it may be concluded that HBr/HCl ratios (by volume of concentrated acids, sp.gr. HCl 1.19, sp.gr. HBr 1.38) from 2 to about 1/3 give equally good results. We have adopted a 1 : 1 ratio, with distillation at 150-160°.

By first distilling from hydrochloric acid solution at 160°, arsenic, antimony and germanium can be removed, so that they do not accompany tin in the hydrobromic-hydrochloric acid distillation. The only element giving trouble is selenium, which partly accompanies tin in the hydrobromic acid distillation and gives a white precipitate or turbidity in the subsequent dithiol determination if its amount is greater than about 10 γ. The remedy for this is precipitation of selenium with sulfur dioxide in the distillate. To assure the formation of a coagulable precipitate, 0.1 mg of Se (IV) is first added.

Before tin can be determined in the distillate, the solution must be evaporated to remove the excess acid. FARNSWORTH AND PEKOLA used hydrogen peroxide to decompose hydrobromic acid. In our hands, this procedure resulted in the loss of tin. Nitric acid was found to be entirely satisfactory for the purpose.

The results in Table IV demonstrate that tin can be satisfactorily separated and determined by the recommended procedure in the presence of arsenic, bismuth,

TABLE IV

PHOTOMETRIC DETERMINATION OF TIN AFTER DISTILLATION

Addition	*Sn taken* γ	*Sn found** γ
30 mg Fe	0.0	0
30 mg Fe	3.0	3.5, 3.5
30 mg Fe	5.0	5.0, 5.0
60 mg Fe	10.0	9.5, 10.0
30 mg Fe	30.0	28.5
100 γ As, 50 γ Bi, 30 mg Fe, 100 γ Mo, 50 γ Sb, 1000 γ W	0.0	0
100 γ As, 50 γ Bi, 30 mg Fe, 100 γ Mo, 50 γ Sb, 1000 γ W	10.0	10.0, 10.0
100 γ As, 50 γ Bi, 30 mg Fe, 100 γ Mo, 50 γ Sb	0.0	0
100 γ As, 50 γ Bi, 30 mg Fe, 100 γ Mo, 50 γ Sb	20.0	19.5
15 mg Fe, 50 γ each Hg, Se, Te	0.0	0
15 mg Fe, 50 γ each Hg, Se, Te	20.0	19.5
12 γ Ru(IV), 10 γ Os(VIII), 10 γ Re(VII)	0.0	0
12 γ Ru(IV), 10 γ Os(VIII), 10 γ Re(VII)	20.0	17.5
0.1 mg Se**	0	0.5, 0.5
0.1 mg Se**	20.0	20.5

* Correction applied for blank (4.0 γ) which was determined by adding 5 γ Sn and deducting (see text). Includes other metals reacting with dithiol, introduced after distillation (chiefly in nitric acid). Since a blank without added tin showed no pink color, the actual tin content is less than $\sim$3 γ.

** Selenium (as selenious acid) added to distillate and precipitation made with sulfur dioxide and hydroxylamine hydrochloride as described under sulfides in PROCEDURE.

TABLE V

DETERMINATION OF TIN IN SILICATE ROCK, IRON METAL, AND PYRITE

Sample	*Method*	*Sn present* *p.p.m.*	*Sn found* *p.p.m.*
Quartz monzonite*	Visual	2.3	2.0, 2.5
	Visual	3.3	3.5
	Photometric	6.3	5.0, 5.0
	Photometric	11	12
	Photometric	21	18.5
	Photometric	31	29
Iron ("Puron")**	Visual	2	2
	Visual	6	6
	Photometric	20	24
	Photometric	40	38
Pyrite***	Photometric	20	20.5

* 1 g sample; original Sn content 1.3 p.p.m. (average of 1.0 and 1.5 p.p.m.); blank in visual method 2 p.p.m. Sn, in photometric method 6.5 p.p.m.

** 0.5 g sample; contained no detectable tin; 0.1% Co, 0.02% Cr, 0.01% Cu added; blank in visual method 1 p.p.m. Sn, in photometric method 9 p.p.m.

*** Leadville, Colo.; 1 g sample; original tin content 0 p.p.m.; selenium separated as described in PROCEDURE.

molybdenum, tungsten, selenium and tellurium in such amounts as are likely to be encountered in silicate rocks, sulfides and meteorites. Table V shows that good recoveries of tin can be obtained from such materials.

When the reagent blank is run in the photometric method, a small amount of tin (3-5 γ) must be added to make certain that the tin concentration in the final solution will be above 3 p.p.m. Below this value, as already mentioned, no coloration is obtained, and it might therefore happen if no tin were added in the blank run that no tin would be shown, although some is present in the reagents and is adding its effect to the tin in the sample. The photometric blank is the sum of the absorbance due to tin and to possible traces of other metals giving colored or slightly soluble products with dithiol. In the present work a blank of 4 γ apparent tin was found with analytical-reagent nitric acid and ordinary distilled water, and of 3 γ apparent tin with nitric acid and water redistilled in Pyrex. By using purified hydrobromic acid, hydrochloric acid, sulfuric acid, and nitric acid, and substituting KH_2PO_4 (5 g) for 85% phosphoric acid, the photometric blank was reduced to 1 γ.

When the blank is run in the visual comparison method, tin need not be added. The blank in the visual method should not exceed 0.5 γ Sn when reagents purified as described are used.

It should be pointed out that a greenish off-color will be obtained in the visual method if the concentration of sulfuric acid is too high. Therefore it is important to fume down to a drop before color development. The final dilution to 0.4-0.5 ml takes care of any small variation in the amount of residual sulfuric acid. It is preferable to treat the standards at the same time as the sample solution so that one can more easily obtain the same final volume of sulfuric acid. The hue of sample and standards should be practically the same.

When the sample contains cassiterite, complete decomposition is not obtained even if the residue from the hydrofluoric-sulfuric acid decomposition is fused several times with sodium hydroxide, as shown by the following results. Finely ground cassiterite-bearing pegmatite (0.5 g) was treated with hydrofluoric and sulfuric acids as described above. The residue was treated with 2-3*M* hydrochloric acid and the insoluble matter was filtered off. It was fused at dull redness with sodium hydroxide in a nickel crucible:

	per cent Sn found		
	(1)	(2)	(3)
After HF + H_2SO_4 decomposition	0.0048	0.0055	0.0056
After 1st NaOH fusion	—	0.15	0.11
After 2nd NaOH fusion	—	0.036	0.039
After 3rd NaOH fusion	—	0.011	0.021
After 4th NaOH fusion	—	—	0.012
Total		0.203	0.188

When 0.5 g of the same sample was first fused with sodium hydroxide or other

flux, followed by hydrofluoric-sulfuric acid treatment, the following results were obtained:

Flux	per cent Sn found		
	NaOH	NaOH + C	NaOH + Na_2O_2
After 1st fusion	0.145	0.14	0.10
After 2nd fusion	0.07	0.07	0.07
Total	0.22	0.21	0.17

This problem was not investigated further, because the method described here is intended for samples containing traces of tin, which are not likely to contain cassiterite.

SUMMARY

Procedures are given for the determination of traces of tin with dithiol (4-methyl-1,2-dimercaptobenzene) by visual color comparison and absorptiometric measurement, with special reference to silicate rocks, meteorites, and sulfides. The sensitivity is 1 p.p.m. Sn with 0.5 g of sample. Tin is separated by distillation of the bromide. Provision is made for the presence of selenium.

RÉSUMÉ

Des procédés sont décrits pour le dosage de traces d'étain, au moyen de dithiol (4-méthyl-1,2-dimercaptobenzène) par comparaison visuelle de la coloration et par mesures absorptiométriques, en particulier dans les silicates, les météorites et les sulfures. La sensibilité est de 1 p.p.m. d'étain pour des échantillons de 0.5 g. L'étain est séparé par distillation de son bromure. Des précautions doivent être prises en présence de sélénium.

ZUSAMMENFASSUNG

Es werden Verfahren beschrieben, um Spuren von Zinn mittels Dithiol (4-Methyl-1,2-dimercaptobenzol) durch visuellen Vergleich der Färbung und durch absorptiometrische Messungen besonders in Silikaten, Meteoriten und Sulfiden, zu bestimmen. Die Empfindlichkeit ist 1 p.p.m. Zinn für Einwaagen von 0.5 g. Das Zinn wird durch Destillation seines Bromids abgetrennt. Bei Gegenwart von Selenium werden spezielle Vorkehrungen getroffen.

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THE COLORIMETRIC DETERMINATION OF THORIUM USING 1-(o-ARSONOPHENYLAZO)-2-NAPHTHOL-3:6-DISULPHONIC ACID

by

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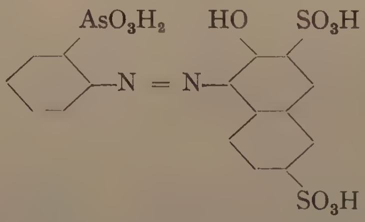
KUZNETSOV[1,2] in 1941 prepared 1-(*o*-arsonophenylazo)-2-naphthol-3:6-disulphonic acid and showed its reaction with thorium ions to form a specific red precipitate. At high dilution the precipitate dissolves and under certain specified conditions the method can be used for the colorimetric determination of thorium. From this work THOMASON, PERRY AND BYERLY[3] developed a method for the determination of thorium in microgram quantities and listed a few of the interferences that may be expected. This and later work[4] showed that 1-(*o*-arsonophenylazo)-2-naphthol-3:6-disulphonic acid is generally specific for quadrivalent ions. The present communication shows the further development of this work with a more detailed account of the interferences which may be commonly encountered in lanthanon analyses and indicates methods by which some of them may be overcome. Details are also given of the spectrophotometric determination of thorium in monazite.

Various trivial names have been proposed for the compound: Thoron, Thorin, Thoronol and Naphtharson. In this country APANS is customary and this is the name which will be used in this paper. All these refer to the same structural formula, which may be represented:



The dye in the form of its di-sodium derivative can now be obtained commercially in this country. Details for its preparation are, however, available[2,6,7].

EXPERIMENTAL

Aqueous APANS solutions containing thorium show an absorption peak at 545 mμ when compared with similar solutions not containing thorium. Spectrophotometric analyses of solutions prepared according to the technique of VOSBURGH AND COOPER[8] indicate that a complex is formed from one atom of thorium and two molecules of APANS. 1 mg of thorium ion was mixed with various amounts of 0.1% aqueous APANS solution, sufficient hydrochloric acid was added to give a final pH of 0.75 and the solutions were diluted to 100 ml with water. These solutions were compared on a spectrophotometer at 545 mμ with similar solutions containing no thorium. The absorption was found to be a maximum when 15 ml of 0.1% reagent were used. This amount was therefore employed for each determination.

100 ml of solution containing 15 ml of 0.1% APANS and various amounts of thorium from 0 to 1.2 mg were adjusted with hydrochloric acid to a pH of 0.75 and the optical densities of the solutions compared with similarly prepared solutions containing no thorium. A graph of "mg thorium" versus "optical density" gave a straight line when a Hilger "Uvispek" spectrophotometer was used at a wavelength of 545 mμ and slit width 0.2 mm. If the same solutions were compared on a Hilger Spekker absorptiometer using the mercury vapour lamp, Calorex heat filters and Ilford 605 filters, the combination recommended for selecting the mercury 546 mμ line, a curved graph was obtained. This flattened considerably above 1.0 mg thorium. The cause of the flattening was found to be due to the transmission of mercury yellow lines at 577 mμ and 579 mμ and this was prevented by inserting Wratten 77 filters together with the above combination. Due to the abnormal thickness of this combination the E-shaped filter container may have to be built out with a thin cardboard.

The graph obtained with this combination is a straight line and enables the drum reading to be converted to "mg thorium" by the use of a conversion factor.

Stability of colour

With pure thorium chloride solutions the complex has been found to be stable for over a month in the cold. If the solutions are heated above 35° C for any length of time decomposition sets in and anomalous results are obtained.

Increases of temperatures from 15° C to 25° C increase the absorption both of the blank and of the thorium-containing solution, when compared with water. The solution containing thorium has, however, a greater temperature coefficient than the blank, so that the net result is an increase in the measurements. A rise in temperature from 15° C to 25° C on a solution containing 0.95 mg thorium as chloride has been found to cause an increase of drum reading of 3.3%.

Effect of pH

The safe limits for acidity lie between pH values of 0.5 and 1.5. Acidities outside these limits cause considerable and sharp diminution of the colour. These limits correspond to an acidity of between 0.5 and 4.0 ml of concentrated hydrochloric acid (11.4*N*) per 100 ml.

METHOD

Reagents

0.1% APANS solution — Dissolve 1 g of 1-(*o*-arsonophenylazo)-2-naphthol-3:6-disulphonic acid (di-sodium salt, as supplied by B.D.H.) in water and dilute to 1 litre in a standard flask.

Diluted hydrochloric acid (1 + 4) — Dilute 200 ml of concentrated hydrochloric acid to 1 litre with water.

Hydroxylamine hydrochloride solution — Dissolve 10 g of hydroxylamine hydrochloride in 100 ml of water.

Phenolphthalein indicator — 1 g of phenolphthalein dissolved in 60 ml of industrial alcohol and 40 ml of water.

Diluted ammonia solution (1 + 1) — Dilute 50 ml of concentrated ammonia solution sp.gr. 0.88 to 100 ml with water.

All reagents should conform to recognized analytical standards.

Apparatus

Hilger Spekker absorptiometer H760 fitted with a mercury vapour lamp and Wratten 77, Ilford 605 and Calorex filters.

Procedure

To the solution containing between 0 and 1.3 mg thorium in a 100 ml volumetric flask add two drops of phenolphthalein indicator and neutralize to a red colour with diluted ammonia solution (1 + 1). Add 10 ml of diluted hydrochloric acid (1 + 4), 5 ml of hydroxylamine hydrochloride solution and 15 ml of 0.1% APANS solution. Prepare a blank solution at the same time containing similar amounts of acid, hydroxylamine hydrochloride solution and APANS only. Make each solution up to the mark and immerse in a thermostat at 25° C for 15 minutes. Measure the solution in 1 cm cells with a Hilger Spekker absorptiometer using a mercury vapour lamp and Wratten 77, Ilford 605 and Calorex filters. Determine the amount of thorium present from solutions similarly prepared with known amounts of thorium.

A solution of pure thorium nitrate containing 0.952 mg thorium has been measured seventeen times by the addition of fresh additions of dye over a period of three months by the same person. An analysis of the results gave the mean drum reading for this solution to be 0.625 with a standard deviation of 0.003, an error of 0.5%.

Effect of interfering cations

The procedure given above was used in the presence of some common cations in order to determine their effect on the drum reading.

i) *Lanthanons.* The effect of adding increasing amounts of lanthanon ions has been investigated. Cerium^{III}, lanthanum, samarium and yttrium interfere by complexing with APANS, the amount of interference decreasing for a given weight of lanthanon in the order stated. Cerium^{IV} bleaches the colour and must be removed with hydroxylamine hydrochloride solution before addition of APANS. Lanthanons alone do not give a straight line graph under the conditions of the procedure except, perhaps, at amounts less than 50 mg of lanthanon. The drum readings are, however, too low to measure accurately within this range. The interference from all the lanthanons can be neglected except for the most accurate determinations if less than 5 mg of lanthanon ion is present.

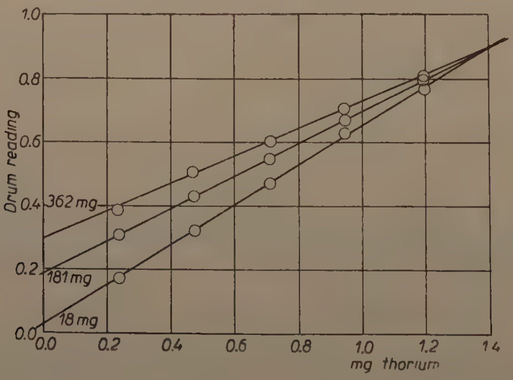


Fig. 1. Effect of mixed lanthanons from monazite (as oxides) on the drum readings of thorium solutions.

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In the presence of constant amounts of lanthanon and varying amounts of thorium two effects are caused —

a) The slope of the graph is altered

b) A positive reading at zero thorium content is obtained.

The effect is shown graphically in Fig. 1.

ii) *Alkali-metals and ammonium.* The effect of lithium, sodium, potassium and ammonium as chlorides on the thorium-APANS complex has been investigated. Each ion causes diminution of the colour but the effect of lithium is considerably greater than the other three (Fig. 2). The effect of the ammonium ion is not recorded as it was considerably less than that of sodium ion.

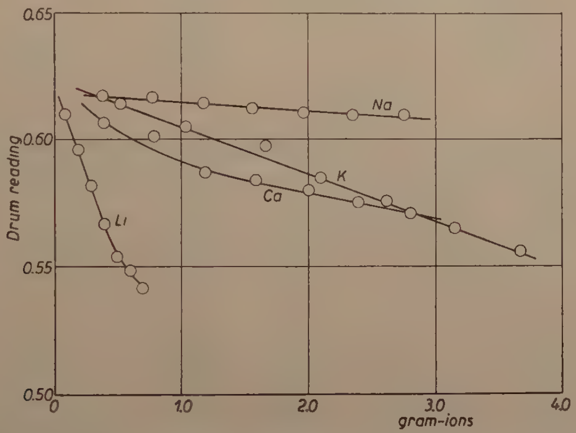

Fig. 2. Interference of lithium, sodium, potassium and calcium ions, on solutions containing 0.95 mg thorium.

iii) *Alkali-earths.* Calcium as chloride causes an interference similar to potassium (Fig. 2). Barium ions cause no interference up to a concentration of about 200 mg barium per 100 ml. At concentrations higher than this an orange-red precipitate appears. This may take as long as an hour to form.

iv) *Iron and aluminium.* A solution of ferric chloride causes considerable interference. The effect can be minimized by reducing the iron to the ferrous state by heating for 10 minutes with hydroxylamine hydrochloride solution. Heating is essential for the reduction to take place. Even under these conditions the effect of iron is considerable and its presence should be avoided wherever possible. The effect of both ferrous and ferric ions is shown graphically together with the effect of aluminium in Fig. 3.

v) *Tin and lead.* Both stannous and stannic chlorides cause strong interference and must be absent. Lead interferes in large amounts by the precipitation of its chloride. It may, however, be tolerated at amounts up to 125 mg lead per 100 ml under the conditions of the procedure before precipitation occurs.

vi) *Zirconium and titanium.* Zirconium forms a red precipitate with APANS which is more insoluble than the thorium complex; it should therefore be absent. The reagent has been used for the determination of zirconium[4]. Titanium interferes similarly.

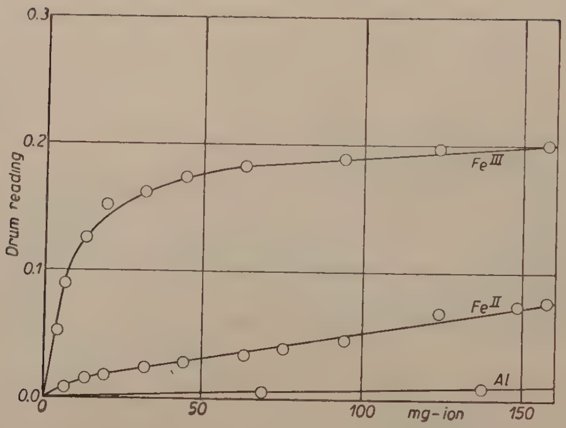

Fig. 3. Effect of ferrous, ferric and aluminium ions on APANS.

vii) *Uranium.* The influence of the uranium (UO_2^{+2}) ion on APANS has been investigated and interference is slight; at concentrations of about 50 mg uranium per 100 ml the effect is equivalent to about 0.2 mg thorium. The effect of uranium^{IV} has been reported previously[3]; it should be absent.

Effect of interfering anions

In general any anion which complexes thorium can be expected to interfere.

i) *Fluoride.* Fig. 4 shows the effect of fluoride on the drum reading of a thorium-APANS complex prepared by the standard procedure and containing 0.95 mg thorium.

The effect of small amounts of fluoride ion can be minimized and almost eliminated by the addition of aluminium ions. Fig. 4 shows that 0.95 mg thorium may be estimated in the presence of as much as 1 mg fluoride by the addition of 10 mg aluminium as the chloride or nitrate. This amount of aluminium is insufficient to cause interference on its own. The drum reading obtained under these conditions corresponds to 0.923 mg thorium, an error of less than 3%. In the absence of aluminium the optical density obtained would correspond to 0.457 mg thorium.

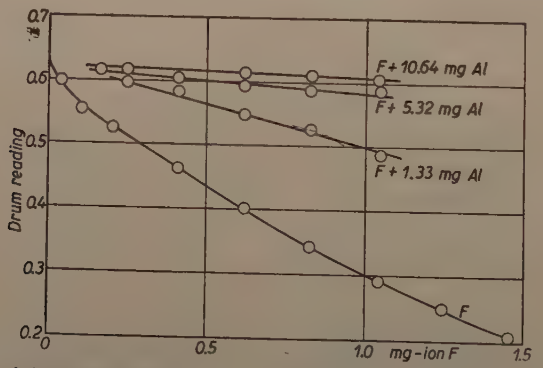

Fig. 4. Suppression of fluoride interference by aluminium ions. Thorium content = 0.95 mg.

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Attempts were made to remove fluoride ion in solutions containing 1 mg thorium and similar amounts of sodium fluoride by fuming with perchloric acid. This was not entirely successful and more consistent results were obtained by fuming with 0.1 g of boric acid as well. The results obtained after the determination of thorium by the standard procedure indicated that although the fluoride was expelled the final drum reading was slightly higher than expected. The experiments were therefore repeated without the addition of thorium and it was found that irrespective of the amount of sodium fluoride taken the drum reading remained the same (Table I).

TABLE I

FUMING OF SODIUM FLUORIDE WITH PERCHLORIC ACID AND BORIC ACID

mg NaF	0	0.4	1.6
Drum reading	0.016	0.015	0.015

Varying amounts of boric acid within the range 0–0.5 g had no effect upon the drum reading. It was therefore concluded that the discrepancies obtained were due entirely to the fuming of the perchloric acid.

The interference disappears if the solution is diluted to a volume and a sufficiently small aliquot taken for determination. An effect in the opposite direction was noticed by HORTON *et al.*[5], who used the interference of the thorium-APANS complex by fluoride ion for the determination of fluorine following a distillation from perchloric acid. He attributed the interference to undecomposed perchloric acid, but it has been noticed that unfumed perchloric acid, whether containing dissolved boric acid or not, does not interfere.

ii) *Sulphate and phosphate.* Phosphate and sulphate both interfere noticeably with the optical density of thorium-APANS complexes. The effect is shown graphically in Fig. 5.

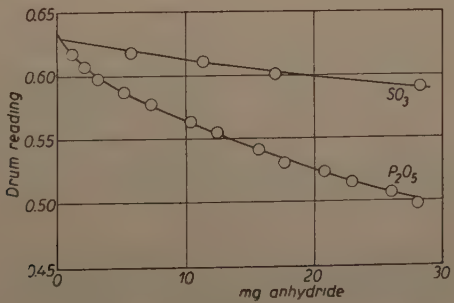

Fig. 5. Effect of phosphate and sulphate on a thorium-APANS complex containing 0.95 mg thorium.

iii) *Nitrate and chloride.* The effect of nitrate ion is extremely slight and for most purposes it can be neglected. About 1.5 g nitrate ion is required to decrease the drum reading by 1%. Chloride ion is completely without effect. However, solutions containing 10 g of sodium chloride have been found to contain a bright red precipitate after standing for twenty-four hours.

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iv) *Sulphur dioxide and sulphites.* It has been found that solutions containing dissolved sulphur dioxide exhibit a red colour similar to that given by thorium ions. Consequently any anion such as sulphite or thiosulphate, which in the acid conditions of the procedure will give sulphur dioxide, can be expected to interfere. If the solutions are allowed to stand for a long period bleaching of the dye occurs and the solutions become colourless. Examination of the absorption of solutions containing sulphur dioxide show a wide absorption band with a peak at 532 mμ.

The interference can be removed by treating the solution before addition of APANS with neutral potassium permanganate solution until the purple colour persists. 0.5 g of hydroxylamine hydrochloride is then added and the procedure completed by the addition of acid and APANS.

v) *Carbon dioxide and carbonates.* Carbon dioxide gas present in the solution with thorium ions and APANS diminishes the red colour of the complex. If any substance which gives carbon dioxide under the conditions of the procedure is believed to be present the procedure should be followed as far as the addition of acid and then the solution should be boiled to expel carbon dioxide. The solution may then be cooled, APANS added, and the procedure completed.

vi) *Organic acids.* These normally interfere when present in large amounts. They may be removed by evaporation of the sample to near dryness with nitric acid with or without the addition of perchloric acid. If perchloric acid is used an aliquot of the final solution must be taken to avoid the interference effect of fumed perchloric acid.

DISCUSSION

It has not been possible to find a method which will separate thorium quantitatively from other interfering ions. In the past it has been thought that oxalate separation was quantitative in the presence of lanthanons which are co-precipitated. This view has recently been shown to be erroneous[9] and work carried out in these laboratories has confirmed these opinions. It has therefore been found advisable not to remove interfering ions by precipitation of thorium but to allow for their effect. If routine analysis for thorium is carried out in the presence of much interference it has been found simplest to determine the amount of interfering ion, increase it by the addition of a measured quantity of a standard solution to a definitely known amount, and use a conversion factor constructed under these conditions. This method has been successfully applied to the determination of thorium in solutions containing phosphate.

The amounts of interfering ions which separately will not interfere with the standard graph or conversion factor are given in Table II.

TABLE II

AMOUNT OF ION CHANGING THE DRUM READING OF 0.95 mg THORIUM BY 0.01

ion	Ce^{III}	Y	Li	Na	K	NH_4	Ca	Ba	Fe^{III}			
mg	6	16	60	2000	600	5000	180	200	0.5			
ion	Fe^{II}	Al	Sn^{II}	Sn^{IV}	Pb^{II}	Ti^{IV}	Zr	U^{VI}	P_2O_5	SO_3	F	NO_3
mg	8.0	170	Nil	Nil	125	Nil	Nil	2	0.8	5	0.02	1500

The determination of thorium in monazite

Experiments were performed on solutions of lanthanons containing thorium to determine the best method for precipitating thorium quantitatively. It has been found impossible to prevent losses occurring by any known method but conditions can be arrived at so as to make the loss a minimum.

The thorium losses on determination with oxalic acid appear to be due entirely to solubility and the use of paper pulp or close-textured filter papers appear to make little difference to the final result. The following method has been developed for the determination of thorium in monazite. Due to lanthanon ions being present in the final solution which is examined spectrophotometrically the "percentage thorium oxide" found is slightly high. This is offset by a thorium loss of about 0.5 mg in the separation with oxalic acid. The combination of these two factors means that the final result is about 0.05 high.

A 'synthetic' monazite has been prepared containing Pb, Fe, Al, U, P_2O_5, Ca, Ce and Th in the proportions present in South African monazite. Using the given method, duplicate determinations on two separate precipitations with oxalic acid gave 5.57, 5.55 and 5.51, 5.55% ThO_2. The true thorium content was equivalent to 5.49% ThO_2.

A South African monazite gave 5.40, 5.37 and 5.40, 5.39% ThO_2.

Results obtained by other methods were:

i) Two precipitations with oxalic acid and final determination by benzoic acid[10]
5.2, 4.8%

ii) Chromatographic method[11] using APANS for final determination
5.36, 5.32%

The monazite is opened with perchloric acid by a modification of the procedure recommended by WILLARD AND GORDON[12].

METHOD

Reagents

Perchloric acid — An approximately 70% w/v solution.

Concentrated hydrochloric acid — 11.4*N*.

Hydrazine hydrochloride — crystals.

Diluted hydrochloric acid (1 + 3) — Mix 80 ml concentrated hydrochloric acid with 240 ml water; this amount is required for each determination.

Diluted hydrochloric acid (1 + 4) — Dilute 200 ml 11.4*N* hydrochloric acid to 1 litre with water.

Bromphenol blue indicator — Dissolve 0.1 g in 250 ml of 20% v/v industrial alcohol.

Concentrated ammonia solution — sp.gr. 0.88.

Concentrated nitric acid — 16.0*N*.

Oxalic acid — crystalline.

Oxalic acid wash liquor — Dissolve 20 g of oxalic acid in water, add 10 ml of concentrated nitric acid and dilute to 1 litre.

All reagents should conform to recognized analytical standards.

Apparatus

250 ml conical flask with a B 29 ground glass socket and an air condenser about 40 cm long with a B 29 cone.

Procedure

Grind the sample so that it all passes through a 120 mesh sieve. Weigh 10 g and transfer to the 250 ml conical flask. Add 40 ml perchloric acid and boil under the reflux air condenser on a hot plate for 3 hours. Conditions should be arranged so that the perchloric acid refluxes about 10 cm below the top of the condenser. Cool carefully, remove the air condenser and add 100 ml of diluted hydrochloric acid (1 + 4). Add slowly with vigorous shaking 4 g hydrazine hydrochloride, then heat to boiling and keep hot for one hour.

Cool the flask under the tap, add three Whatman accelerators, or an equivalent amount of ashless floc, and shake until dispersed. Filter through a 1 cm paper pulp pad using suction. Wash thoroughly with diluted hydrochloric acid (1 + 3) using 200 ml in all. Wash pad twice with small amounts of water. Transfer filtrate to 500 ml flask using the remaining 120 ml of diluted hydrochloric acid (1 + 3) and dilute to the mark with water.

Pipette a 50 ml aliquot into a 250 ml beaker, add a few drops of bromphenol blue indicator and neutralize with concentrated ammonia solution added dropwise until the indicator turns blue. Add 3 ml concentrated nitric acid, stir and dilute to 100 ml. Heat to boiling and add gradually 5 g oxalic acid, stirring continuously. Stir for 2-3 minutes after the addition and allow to stand in a cold water bath for 1 hour or longer. Filter the precipitate on a 12.5 cm Whatman 540 paper and wash with oxalic acid wash liquor.

Transfer the paper and precipitate to the original 250 ml beaker. Add 30 ml concentrated nitric acid and 10 ml perchloric acid. Cover the beaker with a clock-glass and evaporate the contents until the vigorous end reaction has ceased and all traces of filter paper have vanished. Fume gently for 5 minutes. Cool the beaker and wash the contents quantitatively into a 500 ml standard flask. Make up to the mark with water.

Withdraw a 10 ml aliquot by means of a pipette and deliver into a 100 ml standard flask. Determine the thorium content by the procedure given on page 164 but omitting the neutralization to the red colour of phenolphthalein.

$$\begin{aligned} &\%\ ThO_2 \text{ in monazite} \\ &= \frac{\text{mg } ThO_2}{1000} \times \frac{500}{10} \times 100 \\ &= 5 \times \text{mg } ThO_2 \end{aligned}$$

ACKNOWLEDGEMENTS

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SUMMARY

A method is described for the determination of thorium in milligram quantities using 1-(*o* arsonophenylazo)-2-naphthol-3:6-disulphonic acid (APANS) with a precision of 0.5%. An account of the interferences to be expected from some common ions is given and the method is employed in the determination of thorium in monazite following an oxalate separation.

RÉSUMÉ

Une méthode est décrite pour le dosage du thorium (pour des teneurs de l'ordre du mg) au moyen de l'acide 1-(*o*-arsonophénylazo)-2-naphtol-3:6-disulfonique (APANS), avec une précision de 0.5%. L'influence de certains ions courants est étudiée. Cette méthode est utilisée pour le dosage du thorium dans la monazite, après séparation comme oxalate.

ZUSAMMENFASSUNG

Es wird eine Methode beschrieben, um Thorium (in der Grössenordnung vom mg) mit Hilfe der 1-(*o*-Arsonophenylazo)-2-naphtol-3:6-disulphonsäure (APANS) mit einer Präzision von 0.5% zu bestimmen. Der Einfluss gewisser häufiger Ionen wurde untersucht. Diese Methode wird für die Bestimmung von Thorium im Monazit angewandt, nachdem es als Oxalat ausgeschieden worden ist.

References p. 171

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ÉTUDE DU DOSAGE DU PHOSPHORE ET DE L'ARSENIC DANS LES ACIERS PAR COLORIMÉTRIE

par

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I. OBJET DE L'ÉTUDE

1. Mettant à profit les propriétés des hétéropolyacides silico- et phosphomolybdiques, l'on a précédemment[1,2] étudié le dosage colorimétrique du silicium et du phosphore dans les aciers.

L'objet initial de la présente étude est la mise au point d'une méthode de dosage de l'arsenic fondée sur les propriétés parallèles des hétéropolyacides arséniomolybdiques.

2. Une propriété nouvelle découverte au cours de cette recherche, touchant la réduction des hétéropolyacides molybdiques a conduit à revenir sur la question du dosage du phosphore, déjà traitée précédemment.

3. En définitive, le présent travail donne des méthodes nouvelles pour le dosage colorimétrique du phosphore et de l'arsenic dans les aciers.

II. PARTIE BIBLIOGRAPHIQUE

4. S'agissant de doser l'arsenic à l'aide du complexe molybdique, le phosphore doit être séparé préalablement, car dans les milieux d'acidité convenant à la formation et à la réduction de l'acide arséniomolybdique, l'acide phosphomolybdique, qui serait également formé et réduit, donnerait sa coloration bleue propre, qui se superposerait ainsi à celle de l'arsénio-conjugué réduit.

Les techniques classiques prévoient donc la séparation par distillation de l'arsenic; aucun test ne permet cependant de s'assurer que l'arsenic a bien été distillé en totalité, si ce n'est évidemment de répéter à plusieurs reprises la détermination entière, distillation et dosage, et de juger de la réactitude des opérations par la concordance des résultats obtenus.

5. KAKITA[3] a fait connaître une méthode, selon laquelle l'acide phosphomolybdique est extrait sélectivement par l'alcool amylique.

Dans le milieu aqueux résultant de cette séparation, l'arsenic est dosé colorimétriquement au moyen de la coloration bleue du conjugué arséniomolybdique, réduit au moyen de l'hydrazine.

III. PARTIE EXPÉRIMENTALE

6. Il a paru désirable de faire usage, dans cette technique, de l'acide ascorbique, déjà utilisé antérieurement[2], et qui donne des colorations bleues beaucoup plus pures que l'hydrazine.

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Les exemples suivants, représentent l'aboutissement des investigations expérimentales poursuivies sur ce point.

Séparation du phosphore et dosage de l'arsenic en l'absence de fer

Dans 5 béchers (50), distribuer:
10 ml de liqueur de phosphate disodique (1 ml = 10 γ P);
respectivement 0-1-2-3-4 ml de liqueur d'arséniate de sodium (1 ml = 25 γ As);
5 ml de liqueur 5*N* d'acide sulfurique;
respectivement 25-24-23-22-21 ml d'eau; enfin
10 ml de solution de molybdate de sodium (10 g/l) (L'acidité ainsi réalisée est 0.5*N* en acide sulfurique.)
Chauffer à 70-80° (b.m.) pendant 5 à 10 min. Laisser refroidir.
Extraire par un mélange de 75 parties en volumes d'éther et 25 parties d'alcool amylique (deux extractions avec 25 ml, une extraction avec 20 ml du mélange de solvants).

Les phases aqueuses étant reçues en fioles jaugées (100), distribuer successivement: eau q.s.p. 75 ml environ; 3 ml de liqueur 3*N* d'acide sulfurique, 10 ml de solution de molybdate de sodium (10 g/l), 10 ml de solution d'acide ascorbique (2 g/l), et de l'eau pour compléter à 100 ml environ. (L'acidité ainsi réalisée est 0.4*N* en acide sulfurique.)

Porter au bain-marie bouillant 10 min. Refroidir, compléter à 100 ml. Mesures photométriques (λ = 725 mμ). Les résultats sont consignés dans le Tableau I, colonne 1.

Gamme d'étalonnage

Dans 5 fioles jaugées (100), distribuer: liqueur d'arséniate de sodium (1 ml = 25 γ As: 0-1-2-3-4 ml); 8 ml de liqueur 5*N* d'acide sulfurique; de l'eau pour diluer à 85 ml environ; 10 ml de solution de molybdate de sodium (10 g/l); 10 ml de solution d'acide ascorbique (2 g/l) (Acidité réalisée: 0.4*N* en acide sulfurique). Porter au bain-marie bouillant 10 min. Refroidir. Compléter à 100 ml; mesures photométriques. Les résultats sont consignés dans le Tableau I, colonne 2.

TABLEAU I

As	*Mesures photométriques*	
γ	*1*	*2*
100	92 → 100	91.5 → 100
75	74	75
50	49	49
25	24	24
0	0	0

Il y a bien identité, à l'approximation expérimentale près, des mesures de l'arsenic, directement et après extraction.

7. *Remarques.* a) Le choix de l'acidité 0.5*N* en acide sulfurique pour la formation des acides phospho- et arséniomolybdiques résulte d'une étude systématique de l'acidité.

b) D'essais dans lesquels ont été employés, pour l'extraction de l'acide phosphomolybdique, différents solvants: alcool amylique; alcool *iso*butylique et benzène (parties égales); acétate d'amyle et éther (parties égales); alcool butylique normal et chloroforme; 25 parties d'alcool amylique et 75 parties d'éther, c'est cette dernière formule qui s'est montrée la plus efficace pour l'extraction de l'acide phosphomolybdique.

c) Il a été constaté que, dans l'extraction par ce solvant, une partie notable du molybdate mis initialement en oeuvre en vue de la formation des acides phospho- et arséniomolybdiques, se trouve extraite, de sorte qu'il n'en subsiste plus suffisamment dans la phase aqueuse pour développer la coloration bleue du conjugué arséniomolybdique réduit: il faut donc ajouter de nouveau du molybdate de sodium à ce moment du dosage.

d) En présence de fer, celui-ci doit être réduit au stade ferreux, préalablement à la réduction de l'acide arséniomolybdique; afin de ne pas faire usage de quantités trop importantes d'acide ascorbique, une réduction préalable doit être faite, et, après essai du chlorhydrate d'hydroxylamine, de l'acide thiomalique, du trichlorure de titane et du sulfite de sodium, c'est ce dernier qui a été retenu.

8. *Essais en présence de fer.* 1 g de fer est attaqué* et le liquide d'attaque, complété à 250 ml A cinq prises d'essai de 25 ml de ce liquide, ajouter: 10 ml de liqueur titrée de phosphate disodique (1 ml = 10 γ P) et respectivement 0-1-2-3-4 ml de liqueur titrée d'arséniate de sodium (1 ml = 25 γ As). Neutraliser par la lessive d'hydroxyde de sodium (400 g/l) (tournesol). Ajouter successivement:
5 ml de liqueur $5N$ d'acide sulfurique; 10 ml de solution de molybdate de sodium (10 g/l), et de l'eau pour compléter à 50 ml (l'acidité sulfurique réalisée est donc $0.5N$). Chauffer à 70-80° pendant 5 min (bain-marie). Refroidir.

Extraire en ampoules à décantation par le mélange: alcool amylique (25 parties) et éther (75 parties), soit deux extractions par 25 ml, une extraction par 20 ml. Recevoir les phases aqueuses en fioles jaugées de 100.

Distribuer: 5 ml de solution de molybdate de sodium (10 g/l), 3 ml de liqueur $5N$ d'acide sulfurique; 10 ml de solution de sulfite de sodium crist. (100 g/l). Repos 2 à 3 min; 10 ml de solution d'acide ascorbique (30 g/l). Agiter. Compléter à 100 ml avec de l'eau (acidité sulfurique réalisée: $0.4N$). Chauffer au bain-marie bouillant 10 min. Refroidir. Les résultats des mesures photométriques (Tableau II) sont en accord avec ceux du Tableau I.

TABLEAU II

As γ	*Mesures photométriques*
100	93 → 100
75	76
50	49
25	24
0	0

9. On remarque que les termes sans arsenic des gammes sont légèrement colorés en jaune-brun. (Il s'agit sans doute de composés de réduction molybdiques.)

10. *Réduction en présence de bismuth, de titane ou de zirconium.* Si l'on suppose que les sels de ces trois métaux, donnant des complexes phosphoriques, masqueraient ainsi cet acide vis-à-vis de la réaction ceruleo-molybdique, leur introduction permettrait d'éviter l'extraction préalable de l'acide phosphomolybdique; il resterait bien entendu à étudier l'action de ces sels sur l'acide arsénique.

On observe que, pour des doses suffisantes de sels de titane ou de zirconium, les ions arsénio- et phosphomolybdiques, et orthomolybdiques sont en fait réduits *à froid;* au contraire, en présence d'un sel de bismuth, les acides phospho- et arséniomolybdiques et paramolybdique, sont réduits *à froid,* l'acide orthomolybdique lui-même ne l'étant pas.

Il semble que ces faits n'aient pas été signalés jusqu'à présent.

11. Pour les expliquer, l'hypothèse peut être faite, que le bismuth formerait des

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* Attaque selon[2], et *Appendice I* du présent travail.

complexes phosphoriques ou arséniques analogues au molybdate $(MoO_4)_2Bi^-$*, le bismuth ainsi introduit dans la molécule ayant pour effet, en augmentant l'encombrement, de faciliter la réduction de l'ion molybdique. La même explication vaudrait si l'on suppose la formation de zirconimolybdates ou de molybdates de zirconium, et de complexes analogues du titane**.

12. L'action des sels de bismuth, de titane ou de zirconium est précisée par les observations expérimentales suivantes.

5 ml de solution d'acide phosphomolybdique (0.66 g/l d'acide phosphomolybdique; 1 ml = 10 γ P), en milieu d'acidité sulfurique 1.2*N* et en présence de 12.5 mg de bismuth (*cf.* APPENDICES) et d'acide ascorbique (10 mg), sont réduits *à froid* (dilution 50 ml).

Le paramolybdate d'ammonium (solution à 0.59 g/l, correspondant en Mo à celle d'acide phosphomolybdique), dans les mêmes conditions, est réduit *à froid*, plus énergiquement encore que l'acide phosphomolybdique lui-même.

Mais inversement, le molybdate de sodium (solution correspondant à 0.820 g/l), dans les mêmes conditions, n'est pas réduit.

En vue de la réduction des acides phospho- ou arséniomolybdiques, formés per action des acides phosphorique ou arsénique avec l'acide molybdique, des concentrations suffisantes de molybdate de sodium et d'acide ascorbique sont nécessaires. L'optimum est:

— pour le dosage du phosphore: acidité 1.2*N* en acide sulfurique; 10 ml de solution de molybdate de sodium (20 g/l), et 2 ml d'acide ascorbique (30 g/l) pour un volume total de 50 ml.

— pour le dosage de l'arsenic: acidité 0.5*N* pour la formation de l'acide phosphomolybdique; acidité 0.4*N* pour la formation et la réduction du conjugué arsénio-molybdique bleu réduit, avec 5 ml de solution de molybdate de sodium (10 g/l) et 10 ml de solution d'acide ascorbique (30 g/l), pour un volume total de 100 ml.

13. *Réduction du phospho-conjugué en présence de titane ou de zirconium.*

Liqueur de bismuth: *cf.* APPENDICES.

Liqueur de titane ou de zirconium (1 ml = 1 mg de Ti ou de Zr). La quantité pesée de TiO_2 ou de ZrO_2 est attaquée par fusion en creuset de platine par le sulfate acide de sodium, reprendre *à froid* par l'acide sulfurique 5*N*.

A 25 γ de P (2.5 ml de liqueur de phosphate disodique, APPENDICE 1) (cas du bismuth), ou à 50 γ P (cas du titane ou du zirconium) ajouter les quantités variables voulues de liqueurs acides (5*N* en acide sulfurique) de bismuth, de titane ou de zirconium, puis les volumes voulus de liqueur 5*N* d'acide sulfurique (volume total de liqueur de bismuth, de titane ou de zirconium et d'acide sulfurique 5*N* = 12 ml); puis 10 ml de solution de molybdate de sodium (20 g/l), 2 ml de solution d'acide ascorbique (30 g/l) et de l'eau pour compléter à 50 ml. (Acidité des milieux ainsi réalisés: 1.2*N*.)

Dans chaque série, des témoins sont faits, étant exempts de solution phosphorique, afin de vérifier qu'il n'existe aucune réduction du molybdate seul, en l'absence de phosphate.

Les résultats sont consignés dans le Tableau III, p. 176.

Le titane et le zirconium sont à éliminer, comme entraînant la réduction de l'acide molybdique seul; le bismuth doit être employé à dose suffisante pour donner une réduction complète à froid.

14. *Réduction de l'arsénio-conjugué en présence de bismuth, de titane ou de zirconium.* A 50 γ As (liqueur d'arséniate de sodium 1 ml = 25 γ As), ajouter les volumes voulus de solution de bismuth, de titane ou de zirconium, et les volumes voulus de liqueur 5*N* d'acide sulfurique (volume total des liqueurs de bismuth, de titane ou de zirconium, et d'acide sulfurique à 5*N* = 4 ml); puis 5 ml de solution de molybdate de sodium (10 g/l), 5 ml de solution d'acide ascorbique (30 g/l), et de l'eau pour compléter à 50 ml. (Acidité des milieux ainsi réalisés: 0.4*N* en acide sulfurique.) Dans chacun des cas, des témoins sont faits dans lesquels on n'ajoute pas de liqueur d'arséniate (en présence de bismuth, aucun de ces témoins ne donne de coloration avec le molybdate en l'absence d'arsenic). Les résultats sont consignés dans le Tableau IV, p. 177.

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* Traité de Pascal, XI, p. 62.

** *ibid.*, V, p. 739.

TABLEAU III

Bi mg	Mesures photométriques γ = 670 mμ 1 h	2 h	4 h
15	52	66.5	68.5
12.5	46	63.5	67.5
10	46	62.5	67.5
7.5	41	61.5	66.5
5	33.5	57.5	66
2.5	27.5	52.5	64.5
1.25	20	43.5	61.5
1	31	55	59
0.75	21.5	46	55
0.5	15	36	49.5
0.25	7	16.5	32.5
0.125	4	10.5	20
0.0625	4	8.5	16
0	3	6	13

Ti mg	2 h		4 h		6 h	
	Molybdate seul	Molybdate + phosphate	Molybdate seul	Molybdate + phosphate	Molybdate seul	Molybdate + phosphate
12	6.5	12	20	37.5	51.5	95
10	5.5	9.5	16	29.5	41	77
8	3.5	8.5	11	24.5	31	67
6	1	5	7	19.5	22	54
4	0	2.5	4.5	12	17	37
2	0	2	1	11	7	35

Zr mg	3 h		6 h		8 h	
	Molybdate seul	Molybdate + phosphate	Molybdate seul	Molybdate + phosphate	Molybdate seul	Molybdate + phosphate
12	3	13.5	8.5	39	12.5	58.5
10	2	12	6	34.5	9	50
8	2	10.5	5.5	30	7.5	43.5
6	1.5	8.5	4	25	5.5	37.5
4	1	8.5	2.5	25	3.5	35.5
2	0.5	7	1.5	22	2.5	30.5

15. En résumé, seul le bismuth ne donne pas la réaction colorée avec l'orthomolybdate de sodium. Le développement à froid de la coloration bleue des conjugués phosphorique et arsénique est accéléré par des concentrations croissantes en bismuth; c'est pourquoi il est prévu une dose suffisante de cet élément dans les dosages.

16. *Dosage du phosphore.* Le mode opératoire (APPENDICE I) résulte de l'étude antérieure[2] et tient compte des faits nouveaux: introduction de 15 mg de bismuth en milieu d'acidité sulfurique $1.2N$.

L'extraction finale par l'alcool amylique rend la méthode applicable aux aciers de toutes nuances, les éléments d'alliage n'ayant alors plus d'influence sur la mesure colorimétrique, et la coloration parasite mentionnée § 9 se trouvant éliminée.

Mesures à 670 mμ (courbe 1, p. 178). La courbe pour P variant de 0 à 50 γ (densité optique = f(P)), est une droite.

17. *Dosage de l'arsenic.* Dans le mode opératoire (APPENDICE II) l'acidité sulfurique lors de la formation des acides phospho- et arséniomolybdiques est $0.5N$; l'acidité

sulfurique du milieu de la réduction de l'acide arséniomolybdique est 0.4*N*. L'extraction finale par l'alcool amylique est conservée.

Mesures photométriques à 725 mμ (courbe 2, p. 178). La courbe pour As variant de 0 à 100 γ (densité optique = f (As)), est une droite.

TABLEAU IV

Bi mg	*Mesures photométriques*					
	½ h	*1 h*	*1.30 h*	*2 h*	*2.30 h*	*15 h*
2	45.5		45		44.5	
1.5	43		43		42.5	
1	40.5	42	42.5	42.5	41.5	
0.75	36.5	41	42	41.5	40.5	
0.5	35.5	41	41.5	41.5		
0.375	34.5	41	41.5	41.5		
0.25	28.5	38.5	39	39		
0.125	27	37	37.5	37.5		38
0.09375	23.5	36	37.5			37.5
0.0625	18.5	31.5	35			36.5
0.0468	15.5	27.5	34			36
0.03125	11	21	28.5			37
0.0156	7	11.5	17			37.5
0.0075	3	5.5	8			35

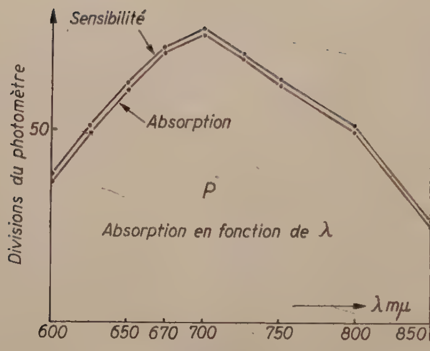
Ti mg	*2 h*		*4 h*		*5 h*	
	Molybdate seul	*Molybdate + arséniate*	*Molybdate seul*	*Molybdate + arséniate*	*Molybdate seul*	*Molybdate + arséniate*
4	30.5	30.5	38.5	49	40.5	55
3	25	23.5	29	39	30	43.5
2	13	15.5	17.5	25	18.5	28
1	7	7.5	8	11.5	8.5	13
0.5	4	4	4	7	4	7.5

Zr mg	*2 h*		*3 h*		*3.30 h*		*18 h*	
	Molybdate seul	*Molybdate + arséniate*	*Molybdate seul*	*Molybdate + arséniate*	*Molybdate seul*	*Molybdate + arséniate*	*Mo seul*	*Mo + arséniate*
4	9.5	23	10	32.5	10	36.5	11	47
3	6.5	21	7.5	29.5	7.5	33.5	8.5	47
2	4.5	14	5	20	5	23	6	41.5
1	3.5	8.5	4	12	3.5	13	4	38
0.5	2	5.5	2.5	8	2.5	9	4	33

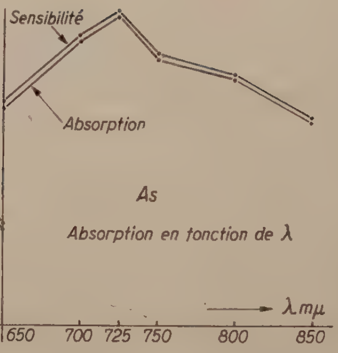
18. Pour justifier la séparation de l'acide phosphomolybdique de l'acide arséniomolybdique par extraction, selon le mode opératoire proposé APPENDICE II, il a été fait appel aux traceurs.

On introduit $^{76}_{33}$As (sous forme d'arséniate), en présence de phosphore (sous forme de phosphate), et l'on détermine l'activité de l'arsenic perdu et entraîné dans la phase organique, après précipitation, de celle-ci, de l'As* sous forme d'arséniate d'argent.

Liqueur de H_3AsO_4 marqué. Dissoudre 20 mg de $^{76}As_2O_3$ (à environ 10 mc par g, soit 0.2 mc) dans 2 ml de liqueur normale d'hydroxyde de sodium et 20 ml d'eau; ajouter 1 ml d'acide sulfurique (1.83) au demi, d'une liqueur de permanganate de



Courbe 1.



Courbe 2.

potassium $N/50$ jusqu'à coloration rose, puis 10 ml de liqueur de sel de Mohr $N/50$ et de nouveau de la liqueur permanganique jusqu'à coloration rose, enfin de la liqueur de sel de Mohr pour décolorer; compléter à 100 ml avec de l'eau (1 ml = 0.2 mg As_2O_3 = 2 μc).

Mode opératoire. Attaquer 1 g de fer pur (réduit par l'hydrogène) par 20 ml du mélange d'attaque perchlorique-nitrique-chlorhydrique (*cf.* APPENDICES), chauffer jusqu'à émission des vapeurs blanches perchloriques, reprendre par 50 ml d'eau, bouillir, transvaser en fiole jaugée de 250 ml, compléter à ce volume avec de l'eau. Dans un bécher de 50, recevoir 25 ml de ce liquide, Ajouter 100 γ de P (2 ml de liqueur de phosphate disodique à 0.580 g/l, dont 1 ml = 50 γ P), et 50 γ d'As (2 ml de liqueur d'arséniate disodique (12) APPENDICE II), puis 1 ml de liqueur As^{76}, soit 200 γ de ^{76}As.

Neutraliser par la solution de soude (400 g/l) (au bleu du tournesol). Ajouter: 5 ml de solution de bismuth (1 ml = 2.5 mg Bi; APPENDICE II (11)), 10 ml de solution de molybdate de sodium (10 g/l), et de l'eau pour compléter au volume de 50 ml environ. Porter au bain-marie (70-80°) pendant 5 min, refroidir.

Faire passer en ampoule à décantation, extraire deux fois avec 25 ml, puis une fois avec 20 ml du mélange de solvants (75 parties d'éther et 25 parties en volumes d'alcool amylique). Rejeter la phase aqueuse.

La phase organique, réunie en bécher (250), est portée au bain-marie pour évaporer l'éther. Ajouter 20 ml d'alcool éthylique, puis 2.5 mg d'As (5 ml de solution d'arséniate disodique à 2.08 g/l, dont 1 ml = 500 γ As); ajouter quelques gouttes d'indicateur bromo-thymol-bleu, puis goutte à goutte la liqueur N d'hydroxyde de sodium jusqu'à virage au bleu de l'indicateur, enfin 5 ml de solution de nitrate d'argent (100 g/l). Tiédir, laisser reposer. Filtrer sur creuset filtrant en verre fritté garni d'une rondelle de papier filtre. Laver avec un mélange de 15 ml d'alcool amylique, 20 ml d'alcool et 10 ml d'eau. Laisser sécher.

Gamme d'étalonnage. Dans deux béchers (100), distribuer 10 et 20 ml de liqueur d'^{76}As à 1 ml = 0.4 γ ^{76}As (Diluer 1 ml de la liqueur précédente à 1 ml = 0.000 2 g ^{76}As, à 500 ml avec de l'eau). Ajouter respectivement 5 ml de solution d'As à 1 ml = 500 γ As soit 2.5 mg d'As). Neutraliser par la liqueur N d'hydroxyde de sodium en présence de B.T.B. comme indicateur, ajouter 5 ml de solution de nitrate d'argent (100 g/l), tiédir, laisser reposer, filtrer et laver comme précédemment.

Chacun de ces deux témoins contient 4 et 8 γ ^{76}As, c'est-à-dire environ 0.04 et 0.08 μc d'activité.

Les activités des filtres, contenant les précipités d'arséniate d'argent, sont mesurées au compteur. Les résultats sont consignés dans le Tableau V.

TABLEAU V

^{76}As γ	*coups min.*
4	1 150 ± 35
8	2 460 ± 49
Essai	1 700 ± 41

D'après celui-ci, il reste environ 5.5 γ de ^{76}As dans la phase organique, pour les 200 γ de ^{76}As mis en oeuvre: la perte en arsenic lors de l'élimination du phosphore par extraction au moyen du mélange alcool amylique — éther peut donc être évaluée à 2.5 à 3% de l'arsenic en oeuvre.

19. L'essai suivant a pour but de vérifier l'absence de phosphore dans la phase aqueuse, après extraction de celui-ci. On introduit du $^{32}_{15}$P (sous forme de phosphate), en présence de phosphate et d'arséniate non radioactifs, et l'on détermine l'activité de la solution aqueuse après extraction, le phosphore radioactif étant précipité sous forme de phosphomolybdate d'ammonium.

Liqueur de ^{32}P. a) 0.5 ml de solution radioactive de phosphate monosodique (à 1 ml = 2 mc, soit 1 mc) sont dilués à 100 ml (1 ml = 10 μc).

b) 1 ml de cette dilution est diluée à 500 ml (5 ml = 1 μc).

Mode opératoire. a) A 25 ml de la solution d'attaque de fer (§ 18, attaque de 1 g de fer, dilution à 250 ml), reçus en bécher (50), ajouter 0.1 mg P (2 ml de liqueur de phosphate disodique à 0.580 g/l, dont 1 ml = 50 γ P) et 50 γ As (2 ml de liqueur d'arséniate disodique (12) APPENDICE II), puis 5 ml de liqueur b) de ^{32}P (soit 1 μc).

Neutraliser par la solution d'hydroxyde de sodium (400 g/l) en présence de tournesol comme indicateur. Ajouter: 5 ml de solution de bismuth (1 ml = 2.5 mg Bi, APPENDICE II (11)), 10 ml de solution de molybdate de sodium (10 g/l) et de l'eau pour compléter au volume de 50 ml environ. Porter au bain-marie (70 à 80°) pendant 5 min, refroidir.

b) Extraire en ampoule à décantation deux fois par 25 ml et une fois avec 20 ml du mélange de solvants (75 vol. d'éther et 25 vol. d'alcool amylique). La phase organique est à rejeter.

c) A la phase aqueuse, ajouter 1 mg de P (2 ml de solution de phosphate disodique à 5.8 g/l, dont 1 ml = 500 γ P), chauffer à 70-80° au bain-marie, ajouter 2 ml de solution d'acide tartrique (500 g/l) et 40 ml de réactif nitro-tartrique-molybdique*. Chauffer à 80-85° pendant 5 min au bain-marie. Laisser déposer, filtrer sur creuset de verre fritté garni d'une rondelle de papier filtre.

Laver au moyen d'une solution nitrique-tartrique de nitrate d'ammonium (Neutraliser de l'ammoniaque (0.925) par de l'acide nitrique (1.33) et en ajouter après neutralisation 1/20 du volume total; diluer au cinquième et ajouter 0.5 g d'acide tartrique).

Gamme d'étalonnage. Diluer 5 ml de liqueur b) de ^{32}P à 500 ml (10 ml = 0.02 μc) (liqueur c).

Dans quatre béchers (100), distribuer:

40-30-20-10 ml de liqueur c de ^{32}P, dont l'activité est:

0.08-0.06-0.04-0.02 μc.

Ajouter 1000 γ P (2 ml de solution de phosphate disodique à 5.80 g/l dont 1 ml = 500 γ P) et opérer selon le mode opératoire (§ c) pour la précipitation.

Les résultats sont consignés dans le Tableau VI. Il résulte de celui-ci qu'il reste dans la phase aqueuse environ 0.03 μc sur 1 μc mis en oeuvre, soit 3 à 4% du phosphore initialement introduit. A remarquer que cette quantité est précisément du même ordre de grandeur que la perte en arsenic (§ 18); ces deux quantités s'équivalent.

La précision de la méthode, d'après ces résultats, peut se chiffrer par $< \pm 2\%$ du chiffre d'arsenic trouvé.

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* Réactif nitro-tartrique-molybdique.

a) Solution de paramolybdate d'ammonium: dissoudre 90 g de ce sel dans 550 ml d'ammoniaque (0.925).

b) Solution nitrique: dissoudre 35 g d'acide tartrique dans 100 ml d'eau et mélanger avec 770 ml d'acide nitrique (1.33).

Le réactif est obtenu en versant la solution a) dans b) et refroidissant; ajouter 0.025 g de phosphate diammonique dissous dans un peu d'eau. Agiter, porter à 80-85° et laisser déposer un jour avant l'emploi.

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TABLEAU VI

^{32}P μc	*coups min.*
0.08	2 280 ± 50
0.06	1 896 ± 45
0.04	1 330 ± 37
0.02	520 ± 32
Essai	980 ± 30 : 0.03 μc

20. *Résultats analytiques.* Les résultats suivants ont été obtenus dans l'analyse des différents aciers (Tableau VII, les colonnes marquées d'un astérisque comprennent les chiffres obtenus par les méthodes décrites en APPENDICE).

TABLEAU VII

Repère	*C*	*S*	*Mn*	*Si*	*Ni*	*Cu*	*Cr*	*P*	*As*	*P**	*As**
1	0.307	0.012	0.503	0.287	0.171	0.164	0.040	0.009	0.046	0.0095	0.045
2	0.234	0.015	0.602	0.276	0.118	0.138	0.050	0.009	0.0497	0.009	0.0505
3	0.17	0.028	0.337	0.113	0.093	0.27	0.049	0.005	0.047	0.0055	0.044
4	0.7	0.025	0.468	0.27	0.134	0.27	0.1	0.033	0.035	0.0315	0.041

APPENDICE I

Dosage colorimétrique du phosphore dans les aciers

Principe — Formation, à la température ordinaire, du dérivé phosphomolybdique bleu réduit.

Réactifs particuliers

1 — Liqueur d'attaque: acide perchlorique (d = 1.61): 75 ml, acide nitrique (d = 1.33): 55 ml; acide chlorhydrique (d = 1.18): 20 ml.
2 — Solution de métabisulfite de sodium (sec R.P.): 200 g/l.
3 — Solution d'hydroxyde de sodium (400 g/l)
4 — Solution de molybdate de sodium (20 g/l)
5 — Solution d'acide ascorbique (30 g/l)
6 — Liqueur de bismuth. Dissoudre 1.440 g de BiO$_2$ par 50 ml d'acide sulfurique (1.83) au $^1/_2$, chauffer jusqu'à obtention d'un liquide limpide. Refroidir. Ajouter 115 ml d'acide sulfurique (1.83). Diluer au litre avec de l'eau.

Autre mode de préparation. Dissoudre 2.1 g de sulfate de bismuth, *à froid* dans de la liqueur $5N$ d'acide sulfurique; compléter au litre avec cette dernière liqueur sulfurique.

La liqueur de bismuth contient 1.25 mg Bi par ml, et son acidité est $5N$ en acide sulfurique.

7 — Liqueur de phosphate disodique: 0.116 g/l (1 ml = 10 γ P).

Mode opératoire

Prise d'essai: 1 g.

1) Attaque par 20 ml du mélange acide (réactif 1) (et 10 ml d'acide chlorhydrique (1.18) dans le cas des aciers inoxydables). Evaporer jusqu'à départ des vapeurs blanches perchloriques. Après refroidissement, reprendre par 30 ml d'eau, porter à l'ébullition. Refroidir. Compléter à 100 ml en fiole jaugée (100).

2) Après avoir filtré s'il y a lieu pour séparer la silice, prélever 10 ml du liquide, que l'on reçoit en bécher (100).

3) Ajouter 10 ml de solution de métabisulfate (réactif 2). Porter à l'ébullition 1 minute (sans dépasser ce temps). Refroidir.

Neutraliser par la solution d'hydroxyde de sodium (réactif 3) jusqu'à précipitation complète du fer (soit 1 ml environ). Ajouter immédiatement 12 ml de solution de bismuth (réactif 6): le précipité d'hydroxyde de fer est entièrement dissous.

4) Ajouter 10 ml de solution de molybdate de sodium (réactif 4), agiter, ajouter 2 ml de solution d'acide ascorbique (réactif 5), agiter, et 4 à 6 ml d'eau. Agiter. Repos 30 min.

5) Faire passer en ampoule à décantation, et extraire une seule fois, par 45 ml d'alcool amylique, en rinçant le bécher avec celui-ci. Recevoir la phase alcoolique en fiole jaugée (50) et compléter à 50 ml avec de l'alcool amylique.

6) *Témoin*

20 ml de liqueur d'attaque (réactif 1) sont évaporés jusqu'à départ des vapeurs blanches perchloriques, reprendre par 30 ml d'eau et compléter à 100 ml avec de l'eau, en fiole jaugée. De ce liquide, prélever 10 ml et continuer selon opér. 3 et suivantes.

7) *Gamme d'étalonnage*

Prise d'essai: 1 g de fer pur (réduit par l'hydrogène)
Attaquer selon opér. 1.
En oper. 2, prélever 6 fois 10 ml que l'on reçoit dans 6 béchers (100).
A chaque prise d'essai ajouter respectivement:
0 — 1 — 2 — 3 — 4 — 5 ml de liqueur phosphorique (réactif 7);
Chaque terme de la gamme correspond donc à:
0 — 0.01 — 0.02 — 0.03 — 0.04 — 0.05% P de l'acier.
Opérer selon opér. 3 et suivantes.

8) *Mesures photométriques*

$\lambda = 670$ mμ. Mesurer la gamme par rapport au terme 0 de celle-ci:
Mesurer chacun des essais par rapport à son témoin.

9) *Calcul*

Le terme 5 de la gamme correspond à 100 divisions du photomètre, soit n divisions lues dans la mesure d'un essai considéré.

$$P\% = \frac{5\,n}{10.000}$$

APPENDICE II

Dosage colorimétrique de l'arsenic dans les aciers

Principe. Formation des acides phospho- et arséniomolybdiques; extraction de l'acide phosphomolybdique par le mélange éther-alcool amylique. Dans la solution aqueuse, formation à la température ordinaire du dérivé arséniomolybdique bleu réduit.

Réactifs particuliers

Les mêmes que pour le dosage du phosphore; en outre:
8 — Solution de sulfite de sodium crist. (100 g/l)
9 — Solution de molybdate de sodium (10 g/l)
10 — Solvant: 750 parties en volumes d'éther-oxyde d'éthyle et 250 parties en volumes d'alcool amylique.
11 — Liqueur de bismuth (1 ml = 2.5 mg Bi dans l'acide sulfurique 5*N*) préparée selon (6) à l'aide de 2.883 g de BiO_2, ou 4.2 g de sulfate de bismuth.
12 — Liqueur d'arséniate de sodium crist. à 0.104 g/l (1 ml = 25 γ As).

Mode opératoire

Prise d'essai 1 g.

1) Attaque par 20 ml de liqueur d'attaque (réactif 1). Evaporer jusqu'à départ des vapeurs blanches perchloriques. Après refroidissement, reprendre par 50 ml d'eau, porter à l'ébullition. Refroidir. Filtrer pour séparer la silice, laver à l'eau chaude. Compléter à 250 ml avec de l'eau.

2) Prélever 25 ml de ce liquide, recevoir en bécher (50). Neutraliser par la solution de soude (400 g/l) (réactif 3) jusqu'à virage au bleu du tournesol.

Ajouter 5 ml de liqueur de bismuth (réactif 11) (le fer précipité à l'état d'hydroxyde est entièrement redissous); 100 ml de solution de molybdate de sodium (10 g/l) (réactif 9) et 6 à 8 ml d'eau. Porter au bain-marie (température des liquides 70 à 80°) pendant 5 min. Refroidir.

3) Faire passer en ampoule à décantation. En lavant le bécher avec 25 ml du mélange de solvants (réactif 10), verser le tout dans l'ampoule à décantation. Agiter, extraire. Répéter l'extraction avec 25 ml du mélange de solvants, puis une troisième fois avec 20 ml.

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Recevoir les phases aqueuses en bécher (100). La phase organique est à rejeter*.

4) Ajouter en agitant après chaque addition: 5 ml de solution de molybdate de sodium (réactif 9); 3 ml de liqueur de bismuth (réactif 11); 10 ml de solution de sulfite de sodium (réactif 8). Repos 2 à 3 min. Ajouter 10 ml de solution d'acide ascorbique (réactif 5) et 20 ml d'eau. Agiter. Laisser reposer 25 à 30 min. La coloration bleue se développe.

5) Faire passer le liquide en ampoule à décantation; laver le bécher par 45 ml d'alcool amylique que l'on reçoit dans l'ampoule à décantation. Agiter, extraire en recevant la phase organique en fiole jaugée de 50 ml. Compléter à ce volume au moyen d'alcool amylique.

6) *Gamme d'étalonnage*

Prise d'essai: 1 g de fer pur (réduit par l'hydrogène).
Attaque par 20 ml de liqueur d'attaque (réactif 1) et opérer selon opér. 1.
Compléter finalement à 250 ml.
Prélever cinq fois 25 ml de ce liquide, recevoir dans 5 béchers (50).
Ajouter respectivement:
0 — 1 — 2 — 3 — 4 ml de liqueur d'arsenic (réactif 12).
Chaque terme de la gamme correspond donc à:
0 — 0.025 — 0.050 — 0.075 — 0.1% As de l'acier
Opérer selon opér. 2 et suivantes.

7) *Mesures photométriques*

$\lambda = 725$ mμ. Mesurer la gamme et les essais par rapport au terme 0 de la gamme.

8) *Calcul*

Le terme 4 de la gamme correspondant à la division 100 du photomètre, soit n divisions lues dans la mesure d'un essai considéré:

$$\text{As }\% = \frac{n}{1.000}$$

Précision ± 2% environ.

RÉSUMÉ

Les acides phosphomolybdique et arséniomolybdique se forment et sont réduits en dérivés de réduction bleus correspondants, dès la température ordinaire, en présence de certains ions métalliques: bismuth, zirconium, titane. Parmi ces ions, les deux derniers catalysent la réduction de l'acide molybdique dans les conditions d'acidité propices à la réduction des seuls acides phospho- et arséniomolybdiques. Le bismuth ne donne pas lieu à cette dernière réaction. Il a été choisi en vue des applications analytiques. Celles-ci concernent le dosage du phosphore et de l'arsenic dans les aciers. Les modes opératoires proposés sont donnés en appendice.

SUMMARY

Phosphomolybdic and arsenomolybdic acids are formed and reduced to their blue reduction products at normal temperature in the presence of certain metallic ions: bismuth, zirconium, titanium. Of these ions, the last two catalyse the reduction of molybdic acid under acid conditions favourable to the reduction of phospho- and arsenomolybdic acids. Bismuth does not bring about this last reaction. It was chosen because of its analytical applications, which are related to the estimation of phosphorus and arsenic in steels. The working methods proposed are given in an appendix.

ZUSAMMENFASSUNG

Die Phosphormolybdän- und Arsenmolybdänsäure werden gebildet und zu ihren blauen Reduktionsprodukten reduziert u.zw., beginnend bei Zimmertemperatur, in Gegenwart von gewissen Metallionen: Wismuth, Zirkonium, Titan. Von diesen Ionen katalysieren die zwei letzten die Reduktion der Molybdänsäure unter den für die Reduktion der Phosphor- und Arsenmolybdänsäure geeigneten Säurebedingungen. Wismuth löst die genannte Reaktion nicht aus. Es wurde für analytische Anwendungen gebraucht. Diese betreffen die Bestimmung des Phosphors und des Arsens in Stahl. Die vorgeschlagenen Arbeitsvorschriften werden im Anhang gegeben.

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* Elle sera récupérée par distillation fractionnée.

THE SPECTROCHEMICAL DETERMINATION OF INDIUM IN CASSITERITE

by

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In an investigation of the geochemical association of indium and tin, it was found necessary to develop a quantitative spectrochemical method for the determination of the indium content of cassiterite specimens. Since major interest was taken in specimens containing greater than 0.001% In, it was not necessary to employ a special procedure to give high sensitivity, such as the double arc method used by SHAW[1] or the chemical enrichment procedure of PROKOPENKO[2]. A fairly simple method using the cathode layer carbon arc has therefore been developed.

According to HARRISON[3] the most sensitive indium lines in the arc are 3039.4 Å (1000), 3256.1 Å (1500), 4104.8 Å (2000) and 4511.3 Å (5000), the numbers in brackets being an indication of the line intensities. Previous workers have generally used In 4511.3 Å or In 3256.1 Å as the analysis line for the determination of indium in mineralogical materials (AHRENS[4]). The use of either of these two lines in the present case was marred by possible interference from Ta 4511.0 Å and Mn 3251.6 Å, since traces of both tantalum and manganese have been present in some of the cassiterite specimens investigated. Although a correction for the manganese interference of In 3256.1 Å can be made (AHRENS and LIEBENBERG[5]) it was regarded as preferable to use In 3039.4 Å as the analysis line. The main possible interfering line in this case is Ge 3039.1 Å. However, since no germanium lines could be detected in any of the cassiterite specimens studied, use of In 3039.4 Å for the determination of indium was regarded as satisfactory.

In order to obtain accuracy and precision, it was necessary to select a suitable internal standard. Since tin in cassiterite has fairly similar volatility and 1st ionization potential to indium, and because its use avoids the addition of an internal standard and possible accompanying errors due to dry mixing, it was decided to employ tin as an internal standard.The line Sn 3032 8 Å was eventually selected with In 3039.4 Å for the analysis pair.

EXPERIMENTAL

All determinations were made using a large Hilger Littrow spectrograph, with quartz optics. Electrodes were made from pieces of 6.5 mm diameter pure graphite rod. The lower cathode electrodes were similarly shaped to those generally employed in cathode layer work, being drilled with a cavity 1/16 in diameter and 4 mm deep. The upper anodes were similar to the cathodes but were undrilled. The optical conditions were such that an intermediate image of the arc was produced on a diaphragm which passed only light from the cathode layer region, this was focused at the collimator by means of a spherical lens near the slit. A 7-step rotating sector was mounted immediately before the slit. A D.C. arc discharge (110 volts on open circuit) carrying a current of 6 amp excited the powdered specimens, and exposures were of 90 sec in each case. Spectra were recorded on Ilford S.R. Panchromatic plates which were developed at 18° C according to directions from the manufacturers.

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Standard mixtures containing 1, 0.1, 0.03162, 0.01 and 0.001 % In were made by thoroughly dry mixing in an agate mortar pure In_2O_3 and SnO_2 in which no indium could be detected. In order to obtain plate calibration and a working curve, a self calibrating procedure was used (AHRENS[4] p. 136). Blackening curves (log-log plots of per cent transmission against relative exposure) of the analysis and internal standard lines and their backgrounds were prepared for the standard mixtures using the step sector and a Hilger non recording microphotometer. The values of the intensities of the lines, obtained from these curves by using a reverse abscissa scale at constant density, were corrected for background, and the ratios of the corrected intensities of the analysis pair were then plotted against per cent indium content on log-log coordinates to give the working curve, Fig. 1. Blackening curves for cassiterite specimens were obtained in the same manner as for the standard mixtures, and from the intensity ratio of the line pair the indium contents could be read from the working curve.

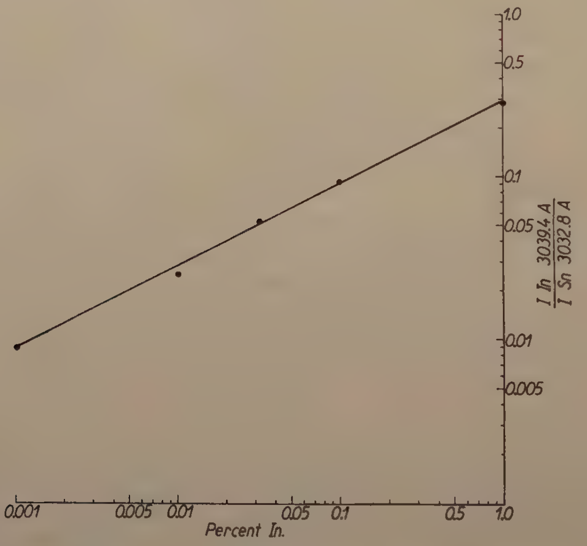

Fig. 1. Working curve for the analysis of indium in cassiterite.

REPRODUCIBILITY AND SENSITIVITY

In the analysis of cassiterite samples the standard deviation incurred was of the order of 5%.

The line In 3039.4 Å was just detectable at a concentration of 0.0001%.

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SUMMARY

In order to determine the indium content of cassiterite specimens, a spectrochemical method, using tin as internal standard and the cathode-layer carbon arc, has been employed. The precision of the procedure is approximately 5 %.

RÉSUMÉ

Une méthode spectrochimique (à arc), utilisant l'étain comme étalon interne, et des électrodes de graphite, est proposée pour le dosage de l'indium dans des échantillons de cassitérite. La précision est d'environ 5%.

ZUSAMMENFASSUNG

Es wird eine spektrochemische Methode (Bogenspektren) vorgeschlagen, welche Zinn zum internen Vergleich und Graphitelektroden verwendet, um Indium in cassiterithaltigen Substanzen zu bestimmen. Die Präzision ist ungefähr 5%.

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THE HETEROMETRIC MICRODETERMINATION OF SULFURIC ACID AS BARIUM SULFATE. A GENERAL STUDY

by

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INTRODUCTION

The determination of sulfuric acid by precipitation as barium sulfate is a reaction which has been most extensively studied in the past. Although no better method is known for the determination of sulfuric acid, this method has many disadvantages. The solubility product of barium sulfate is $1.0 \cdot 10^{-10}$. Its solubility is increased in strong acid solution and the determination must be carried out gravimetrically. If precipitated from a solution which contains other electrolytes the danger exists of interference by adsorption.

The adsorption phenomena in connection with barium sulfate have been studied extensively and are classics in this field. Since in heterometry[1,2] we have very rarely experienced interference by adsorption, we were interested in studying the case of barium sulfate and establishing the extent of interference by adsorption in this reaction. In the course of this study various phenomena occurred which seemed to us to be very instructive. Many experiments, although having no direct bearing on the immediate analytical aspect, were carried out in order to obtain a deeper insight into the phenomena.

From the material presented it is apparent that the heterometric determination of sulfuric acid proceeds quickly if carried out under appropriate conditions. Generally the end-point of the titration could be fixed without difficulty and the error was 0-3%. In almost all cases, after the first maximum density point, an exactly horizontal optical density line was obtained with no further change of density on the addition of excesses of titrant (= barium nitrate). This is so even in many cases where interference, which may be caused by adsorption, does occur. This interference is expressed by a displacement of the end-point of the titration, which appears either too early or too late, depending on whether the interference is caused by the cation or the anion of the supplement.

Generally it may be said that interference by adsorption was established by us only in particular cases, *i.e.* in the presence of excess of K^+, Fe^{+3}, NO_3^- or PO_4^{-3}, and then only if the concentration of the interfering cation or anion was many times greater than the molar concentration of the sulfuric acid which was determined. No interference was encountered in the presence of various bivalent cations at a concentration of $0.1M$ when the concentration of the sulfuric acid was $0.006M$; this means at a molar ratio of 16.6 : 1.

The difference in the behaviour of K^+ and NH_4^+ is remarkable. In the presence of the latter, no interference was observed. In contrast to $FeCl_3$, the presence of 0.1M $AlCl_3$ did not interfere. In all cases with interfering ions, no interference occurred if the concentration of the ion was below 0.02M.

As far as the working conditions are concerned, the following may be said. When dilute aqueous sulfuric acid alone is titrated with barium nitrate, the heterometric titration becomes impossible as the sediment accumulates locally and no analytical end-point is obtained. It was found that a minimum amount of ethyl alcohol changes the titrating conditions entirely: the titration runs smoothly and a sharp end-point is obtained. A titration may thus be completed in ten minutes. If hydrochloric acid is present, the optimum amount of alcohol to be present is 15%-20%. The maximum optical density then decreases with the further increase of the alcohol concentration. The greater the amount of alcohol present, the greater the amount of hydrochloric acid which has to be added in order to work at optimum conditions. The influences of alcohol and hydrochloric acid work in opposite directions and identical results may be obtained with different alcoholic solutions under appropriate acid conditions.

One disadvantage which is common to most of the pure inorganic heterometric determinations is the relatively low sensitivity of the reaction. In this case, the lower limit of concentration of sulfuric acid which can be successfully titrated is $1\text{-}2 \cdot 10^{-3}M$. Using organic reagents such as α-nitroso-β-naphtol or dimethylglyoxime[3], a salt solution which is at least ten times more dilute may easily be titrated heterometrically with precision.

EXPERIMENTAL

The same apparatus was used and the same working conditions observed as in previous heterometric investigations[1-3]. In special cases only coloured filters were used in the presence of solutions which contained coloured foreign salts. In all experiments without exception, where an alcoholic solution was used, the percentage of alcohol (per volume) of the titrated solution and the titrant was always the same.

The temperature of the reacting solutions were thermostatically controlled at 20° C during all the heterometric titrations. This was done only to ensure that the experiments were carried out under similar working conditions, as temperature control is generally unnecessary when working at room temperature. The velocity of stirring was the maximum consistent with stable measurements and was controlled electronically, being more or less uniform in all experiments.

The reagents used were either analytical reagent or chemically pure. Ordinary distilled alcohol was used throughout this investigation. The total volume of the solution was 10 ml at the beginning of each experiment. In all experiments, without exception, the precipitation of barium sulfate began almost immediately upon the addition of the first drop of the titrant.

In most cases the analytical end-point of the titration was fixed directly by the intersection of a line drawn through the points of the last part (= last quarter) of the titration curve with the horizontal maximum density line. In some cases, *i.e.* in the presence of interfering supplements salts or acids, the location of the end-point became less sure (it was difficult to decide whether the above intersection point or the first contact point of the curve with the horizontal line had to be chosen). The value given in the Table is then only an approximation and is designated by an asterisk. In even less certain cases a question mark is placed after the value.

RESULTS AND CONCLUSIONS

a. *Influence of the medium*

It has already been mentioned that working in alcohol-water mixtures yielded better results than working in pure water solutions. In the latter case, the optical

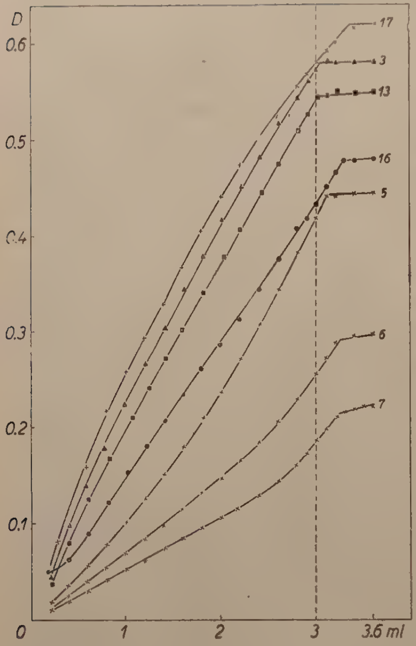

Fig. 1
Titration curves of sulfuric acid with barium nitrate

density values obtained were lower and the results were not definite. Thus working with the maximum amount of sulfuric acid (3 ml $0.02M$) in aqueous solution no certain maximum density point was obtained and the density value was about one-third of the value which was obtained in the optimal alcoholic-water mixture. The influence of these mixtures on the velocity of chemical reactions has been discussed more extensively elsewhere[4]. Table I, Experiments 1-7 (and Fig. 1) show the influence of increasing amounts of ethyl alcohol on the heterometric results. Between 10% and 20% alcohol, no difference in the results could be detected in the absence of hydrochloric acid. On further increasing the amount of alcohol, the maximum optical density gradually decreased. At the same time the errors became greater and the end-point was displaced beyond that calculated. Experiments 9 and 10 show that the addition to the 20% alcoholic solution of hydrochloric acid in a somewhat larger amount, decreased the maximum optical density values and that the analytical end-points which were obtained too early, were uncertain. The results which are obtained in the presence of hydrochloric acid in 50% alcoholic solutions (expts. 11-15) are clearer and very interesting. If these results are compared with those of experiment 7, it can be seen that the addition of hydrochloric acid counteracted the deteriorating effect of larger amounts of alcohol. On increasing the acid concentration, optimal working conditions were soon obtained. Thus hydrochloric acid may be present in solution in high concentration ($0.4N$). Perchloric acid acts like hydrochloric acid (expt. 18).

Experiments 19-23 show results obtained with extremely low quantities of sulfuric acid. Even an $0.0015M$ sulfuric acid solution could still be titrated (expt. 22) in 50% alcoholic solution in the presence of $0.05N$ hydrochloric acid, and the error was normal.

b. *Influence of supplements*

Influence of acids. These experiments were all carried out in 50% alcoholic solution which also contained sufficient hydrochloric acid to give optimum working conditions. Tables I and II and Fig. 1 and 2 show some of the results obtained in the presence of mono- and polybasic acids. When *nitric acid* was used instead of hydrochloric acid (expts. 16 and 17) large errors were found. Although the maximum density values were as usual, the analytical end-points obtained were too late and excesses of barium nitrate were used for the titration. Probably, barium nitrate is coprecipi-

TABLE I

General composition: 3 ml H_2SO_4 $aM + b$ ml alc. + $(6-b)$ ml H_2O +
1 ml acid + x ml $Ba(NO_3)_2$ aM alc. Temp. = 20° C

Expt. No.	*Solutions*				*Found*			
	molarity ($= a$)	*% alcohol*	*acid* *name*	*acid* *normal*	*ml* $Ba(NO_3)_2$ ($= x$)	*Max. opt. density value*	*Approx. titration time (min)*	*% error*
1	0.02	10	—	—	3.07	0.53	7	2.3
2	0.02	15	—	—	3.00	0.50	9	0.0
3	0.02	20	—	—	3.02	0.58	5	0.7
4	0.02	25	—	—	3.06	0.47	6	2.0
5	0.02	30	—	—	3.12	0.41	8	4.0
6	0.02	40	—	—	3.25	0.30	12	8.3
7	0.02	50	—	—	3.26	0.22	9	8.6
8	0.02	20	HCl	0.5	3.00	0.44	12	0.0
9	0.02	20	,,	1.0	2.87	0.40	9	−4.3
10	0.02	20	,,	2.0	2.5	0.29	27	10.0
11	0.02	50	,,	0.5	3.16	0.35	9	5.3
12	0.02	50	,,	1.0	3.04	0.46	7	1.3
13	0.02	50	,,	2.0	3.02	0.55	5	0.7
14	0.02	50	,,	3.0	3.10	0.53	12	3.3
15	0.02	50	,,	4.0	3.03	0.57	12	1.0
16	0.02	50	HNO_3	1.0	3.3	0.48	5	10.0
17	0.02	50	,,	2.0	3.34	0.60	15	11.3
18	0.02	50	$HClO_4$	2.0	3.10	0.60	9	3.3
19	0.005	20	—	—	2.95	0.19	13	−1.6
20	0.005	20	HCl	0.5	2.9	0.14	20	−3.3
21	0.005	50	—	—		0.05	13	
22	0.005	50	HCl	0.5	2.94	0.19	13	−2.0
23	0.005	50	,,	2.0	2.78	0.21	26	7.3

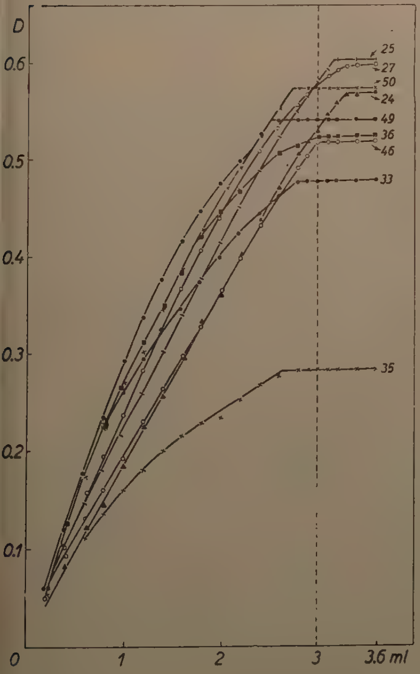

Fig. 2. Titration curves of sulfuric acid with barium nitrate.

tated together with the barium sulfate. Apparently, this phenomenon does not interfere with the character of the particles which absorb the light. No improvement was observed when nitric acid was added *in addition* to the optimal amount of hydrochloric acid (Table II, exp. 27). In contrast to this, perchloric acid had no influence (expt. 28). Neither a 0.1M *acetic*, nor a 0.1M *citric* acid (expts. 29 and 30) had any influence on the results. In contrast to this, *phosphoric* acid had a deleterious effect in a similar direction to nitric acid: more barium nitrate had to be used for the titration although the maximum density value remained as high as usual. If a 0.1N phosphoric acid was used instead, there was no deteriorating effect, and normal results (expt. 26) were obtained.

Influence of polyvalent cations. The results obtained with trivalent cations were

TABLE II

General composition: 3 ml H_2SO_4 0.02M + 1 ml HCl 2N + 1 ml supplements + 5 ml alc + x ml $Ba(NO_3)_2$ 0.02M, 50% alc. Temp. = 20° C

Expt. No.	*Supplement*	*Found*				
		ml $Ba(NO_3)_2$ (= x)	*Maxim. opt. density value*	*Approx. titration time (min)*	*% error*	*Remarks*
24	H_3PO_4 *M*	3.30	0.57	17	+10.0	
25	,, 0.66*M*	3.15	0.60	9	+5.0	
26	,, 0.33*M*	3.06	0.52	11	+2.0	
27	HNO_3*M*	3.3*	0.60	13	+10.0	
28	$HClO_4$	2.98	0.61	11	−0.7	
29	Acetic ac. *M*	3.07	0.56	5	+2.3	
30	Citric ac. *M*	3.05	0.56	6	+1.7	
31	$AlCl_3$ *M*	3.0	0.54	12	0.0	
32	$CrCl_3$ *M*	?	0.30	15		
33	,, 0.5*M*	2.76*	0.48	16	−8.0	
34	,, 0.2 ,,					big flakes
35	$FeCl_3$ 0.5*M*	2.64*	0.28	30	−12.0	with red filter
36	,, 0.2 ,,	3.00	0.52	14	0.0	
37	0.5 ml $FeCl_3$ 0.5*M* + 0.5 ,, Citric ac. 2*M*	2.6?				agglomeration
38	0.5 ml $FeCl_3$*M* 0.5*M* + 0.5 ,, H_3PO_4 *M*	2.8*	0.46	12	−6.6	
39	$MgCl_2$ 2*M*	2.96	0.53	20	−1.3	
40	$ZnCl_2$ *M*	3.04	0.53	17	0.0	
41	$CoCl_2$ *M*	3.06	0.59	13	+2.0	
42	$Co(NO_3)_2$ *M*	3.16	0.51	21	+5.3	
43	$Ni(NO_3)_2$ *M*	3.07	0.63	7	+2.3	
44	$MnCl_2$ *M*	3.00	0.52	10	0.0	
45	$Cd(NO_3)_2$ *M*	3.04	0.55	18	+1.3	
46	$CuCl_2$ *M*	3.00	0.52	20	0.0	
47	NaCl 2*M*	2.92	0.60	9	−2.7	
48	NH_4Cl 2*M*	2.97	0.54	15	−1.0	
49	KCl 2*M*	2.52	0.54	11	−16	
50	,, *M*	2.75	0.58	9	−8.3	
51	,, 0.5*M*	2.90	0.57	14	−3.3	
52	,, 0.2*M*	2.95	0.59	12	−1.7	

different. A 0.1*M* *aluminium chloride* (expt. 31) had no influence whatever whilst iron and chromium chloride both interfered. *Chromium chloride* lowered to some degree the maximum density values (expts. 32 and 33) and less barium nitrate was then necessary for the titration. In addition, the location of the end-point was unsure. If present in lower concentration (expt. 34) flakes were formed and the titration became impossible. *Iron chloride* when present in a concentration of 0.05*M* (expt. 35) $[Fe^{+3}]$: $[SO_4^{-2}]$ = 9 : 1) depressed the maximum density value very considerably and *less* barium nitrate than calculated was used for the titration. Both chromium and iron apparently consume the sulfate anion which was coprecipitated as salt together with barium sulfate and therefore less sulfate was available for the titration. It is very interesting that iron chloride which was present in 0.02*M* concentration ($[Fe^{+3}]$: $[SO_4^{-2}]$ = 3 : 1) no longer influenced the normal titration (expt. 36). Neither the presence of citric nor phosphoric acids (expts. 37 and 38) improved the results in mixtures of these acids with iron. In the latter case the iron and the phosphate ions acted in opposite directions and as a result somewhat less barium nitrate than calculated was used for the titration, thus indicating that the effect of iron prevails. Therefore, it may well be that if the concentration of both ions were properly balanced, no disturbance would occur. An attempt was made to titrate the iron using a red filter but improved results could not be achieved, (expt. 33).

Influence of bivalent cations. As Table II shows, the different bivalent cations, almost without exception, had no influence on the results, if they were present in solution in a 0.1M concentration ([Me] : [SO_4^{-2}] = 16.6 : 1). It is interesting to note that the cadmium and the nickel (expts. 43 and 45) were present as *nitrates*, but nevertheless the influence of the anion was not perceptible. Only in the presence of cobalt did interference occur (expt. 42), but this interference probably differs from that of other interfering cations because more barium nitrate was used for the titration instead of less, as usual.

Influence of monovalent cations. Only the alkali metals were tested. *Sodium* and *ammonium* chlorides (expts. 47 and 48) in 0.2M concentration had no influence on the results. In contrast to these was the behaviour of *potassium* chloride (expts. 49 and 50). Here too, as with iron, a distinction must be drawn between the influences caused when potassium chloride was present in lower and in higher concentrations. In the latter case, less barium was used at the end-point for the titration, although the maximum density value did not change (in contrast to iron!). When the potassium chloride was present in lower concentrations (expt. 52) (= 0.02M) ([K^+] : [SO_4^{-2}] = 3 : 1) it did not interfere any more.

DISCUSSION

If the results which are obtained in the presence of disturbing cations or anions are summarized, it can be seen that interference occurs only when the ions are present in a molar concentration *many* times greater than that of the sulfate anion. This interference is no longer perceptible at the molar ratio of [ion] : [SO_4^{-2}] = 3 : 1 and it can therefore be assumed that the interference is not caused by adsorption but that coprecipitation occurs. This is clearly shown in the following cases: phosphoric acid consumed barium ions being coprecipitated as barium phosphate, and therefore *more* barium was used than calculated for the titration. Potassium ions consume sulfate anions being coprecipitated as potassium sulfate and therefore *less* barium was used. In contrast to this the ammonium cation did not interfere because of the high solubility of ammonium sulfate. The nitrate anion is coprecipitated as barium nitrate and *more* barium was used for the titration. As the ferric ion did not interfere at somewhat lower concentrations, it must be assumed that in this case also, interference by coprecipitation as iron sulfate (anhydrous?) occurred. The problem as to why the bivalent cations did not interfere by coprecipitation still remains to be clarified.

The influence of alcohol-water mixtures and the opposing effect of hydrochloric acid and ethyl alcohol in such mixtures, is more complicated[4-5]. Some time ago the effect of alcohol water mixtures on the velocity of chemical reactions, was studied by one of us (M.B.)[4]. This would be a parallel case to the precipitation of barium sulfate and the effect of alcohol on the particle size. It was then found that alcoholic-water mixtures which contain less than $\sim$ 25% alcohol still act as pure water solutions. In contrast to this, a 50% alcoholic solution acts as a *mixture* of alcohol and water. The effect of hydrochloric acid may therefore be explained as binding the free alcohol molecules and thus cancelling the deteriorating effect of excess of ethyl alcohol. Working in 50% alcoholic solution, which contains hydrochloric acid, the heterometric titrations can be carried out successfully in the presence of high concentrations of strong acid.

Analytical aspects

Apart from a few exceptional cases, sulfuric acid can easily be titrated with barium nitrate in strong hydrochloric acid 50% alcoholic solution. A titration takes about 10 minutes, at room temperature, and the error is 0-3%. 10 ml of a sulfate solution containing 1.5-6 mg sulfuric acid is necessary for a titration.

The presence of phosphate, nitrate, ferric, chromium(III) or potassium ions interferes with the results, but if they are present in a molar ratio of $\leqslant 3$ to 1 $[SO_4^{-2}]$ no interference occurs.

Analysis

Technique. Barium nitrate is added drop by drop from a 5 ml microburet (0.01 ml) and the solution is stirred vigorously. The precipitation begins immediately and the readings on the galvanometer are taken only when they become constant, which generally takes a few seconds to a minute. An enlarged titration curve is drawn which has as abscissa the density values measured, and as ordinate the volume of barium nitrate added. The end-point is obtained by the intersection of the line of the last part (the last quarter) of the titration curve with the horizontal maximum density line.

Method. 5 ml aqueous solution containing a few mg sulfuric acid (or sulfate) and 1 ml 2*N* hydrochloric acid is mixed with 5 ml alcohol. The solution is titrated heterometrically with a 50% alcoholic solution of 0.01-0.02*M* barium nitrate. Titration time is 10 minutes. Error 0-3%.

SUMMARY

The influence of the medium on the precipitation of barium sulfate both in the presence and in the absence of various concentrations of acids, was studied.

The coprecipitation, which occurs in the presence of varying concentrations of phosphoric and nitric acids, as well as in the presence of iron(III), chromium or potassium ions, was studied quantitatively.

A quick method is presented for the micro-determination of sulfuric acid.

RÉSUMÉ

L'influence du milieu sur la précipitation de $BaSO_4$ a été étudiée, en l'absence et en présence de diverses concentrations d'acides. La coprécipitation, qui apparaît en présence de différentes concentrations d'acides phosphorique et nitrique, ainsi qu'en présence des ions du fer(III), du chrome et du potassium, a été étudiée quantitativement. Une méthode rapide est proposée pour le microdosage de l'acide sulfurique.

ZUSAMMENFASSUNG

Der Einfluss des Milieus auf die Abscheidung von Bariumsulfat in An- sowie Abwesenheit von Säuren verschiedener Konzentrationen wurde studiert.

Die Kopräzipitation, welche in Anwesenheit von verschieden konzentrierter Phosphor- und Salpetersäure sowie von Eisen(III), Chrom- und Kalium-Ionen stattfindet, wurde quantitativ verfolgt.

Eine rasche Methode für die Mikro-Bestimmung von Schwefelsäure wurde vorgeschlagen.

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THE FLOWING MERCURY ELECTRODE IN POLAROGRAPHY. PART I

by

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Polarographic studies in hydrofluoric acid media were first reported by CLIFFORD AND BALOG[1] in 1951. These investigators prepared a dropping mercury electrode from a rod of polytrifluorochlorethylene by drilling, softening and drawing down to size on a 0.03 mm tungsten wire mandrel. Considerable difficulty was experienced in carrying out this process and the resulting capillary failed to give a consistently reproducible drop time, tending to produce a spray rather than discrete mercury drops. An alternative electrode was prepared consisting of a platinum tube of small bore embedded in a sheath of polytrifluorochlorethylene. This electrode also failed to yield a consistently reproducible drop time and furthermore possessed some of the undesirable features of noble metal electrodes. Nevertheless, the practicability of using rotating micro-electrodes of platinum and nickel in hydrofluoric acid media was subsequently explored by SARGENT, CLIFFORD AND LEMMON[2] in 1953 with some measure of success. However the polarographic phenomena associated with solid microelectrodes have yet to be subjected to a satisfactory mathematical interpretation; a new approach to the problem of electrode design for hydrofluoric acid media was therefore attempted by the authors.

A small number of dropping electrode capillaries were prepared by drawing down in a flame standard polyethylene tubing of of 12 mm bore, 6 mm wall. This technique yielded a number of serviceable electrodes giving reproducible drop times initially, but after a period of use these electrodes tended to develop drop times which were both extended and erratic. Capillaries having walls of varying lengths and thickness were prepared and tested, but the tendency for lengthening of the drop time appeared to be independent of the dimensions of the capillary wall. The persistence of the erratic behaviour led to the abandonment of further development work on polyethylene dropping mercury electrodes, and attention was focussed on the Heyrovsky streaming mercury electrode[3] as a possible alternative. The design of this electrode was particularly attractive for hydrofluoric acid polarography since the mercury nozzle could be readily fabricated in polyethylene or polytrifluorochlorethylene. However, the stirring of the solution caused by the passage of the jet of mercury, together with the heavy mercury consumption, were factors which could not be ignored in assessing the potentialities of the streaming mercury electrode.

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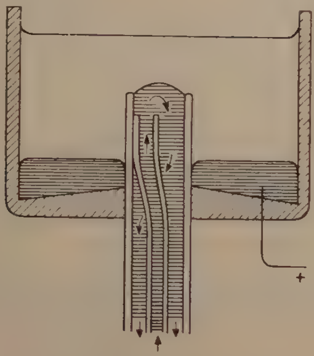

Fig. 1. Polarographic cell with flowing mercury cathode.

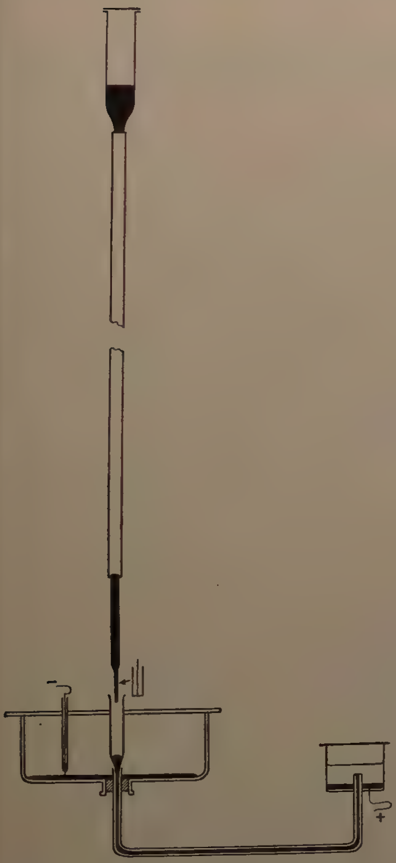

Fig. 2. General arrangement of polarographic cell, amalgam reservoir and dropping mercury electrode assembly.

Consideration was also given to other types of electrodes; but no design yet published was found to be entirely suitable for accurate fundamental polarographic studies in hydrofluoric acid media. Simonnin and Quintin[4] had employed a mercury column renewed by a succession of mercury drops falling from a capillary; Leveque[5] had allowed mercury to flow down the surface of an amalgamated platinum wire; Cooke[6] used an amalgamated silver wire which was rotated at high speed; Lee[7] had devised a rotating mercury electrode, while Streuli and Cooke[8] had studied the characteristics of the stationary mercury pool electrode. The design of the latter electrode seemed particularly suitable at first but unfortunately the diffusion layer tended to increase in thickness with time and, of course, the surface of the mercury pool was not renewed.

It was therefore decided that an attempt should be made to design a new electrode suitable for use in hydrofluoric acid media and combining the advantages of the streaming and dropping mercury electrodes. It was felt that such an electrode should possess a constant surface area but with a renewable surface; the mercury consumption should be economical and the movement at the mercury-electrolyte interface should be as small as possible. Simplicity of design was essential in order that the electrode could readily be fabricated in polyethylene or polytrifluorochlorethylene. To simplify the mathematical interpretation of the polarographic waves it was considered desirable that the reducible ionic species should reach the electrode by diffusion only, unassisted by stirring or convection currents. The requirement of a renewable surface restricted the choice of electronic conductor to mercury or amalgam; mercury was selected for the initial design. A constant surface area could be assured by containing the mercury within an open vertical tube of uniform bore; in order that the surface layer of the mercury should be renewed with the minimum disturbance the fresh mercury would be supplied from a source located within the mercury column. These considerations led to the development of the electrode in Fig. 1, known as the flowing mercury electrode[9].

DESCRIPTION OF ELECTRODE

A column of mercury is contained within a vertical polyethylene tube of 2 mm bore, 0.5 mm wall thickness. The surface layer of the column is continuously renewed by means of a stream of pure mercury issuing from an internal supply tube of 0.5 mm bore, 0.25 mm wall thickness. Control of the fresh mercury supply is exercised by means of an orthodox glass dropping mercury electrode assembly (Fig. 2) from which mercury flows at the desired rate into a funnel connected to the internal supply tube (Fig. 3). A pressure head in the funnel of approximately 10 mm Hg is sufficient to produce the required rate of flow of mercury through the internal supply tube to the electrode surface. The displaced amalgam passes through the annular space surrounding the internal supply tube and finally returns to a reservoir of large surface area. The potential of the polarizable electrode is applied by means of a platinum wire in contact with the amalgam in the reservoir.

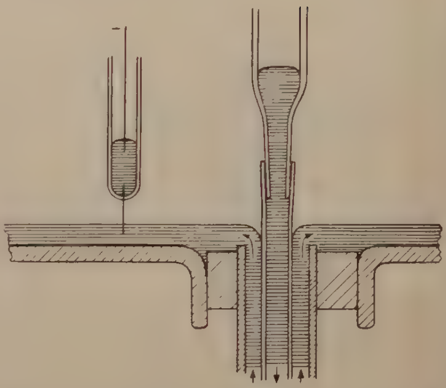
Fig. 3. Arrangement of the mercury supply tube within the electrode tube at the junction with the amalgam reservoir.

The non-polarisable electrode consists of a mercury pool in the base of a polyethylene cell surrounding the polarizable electrode. The pool potential is applied by means of a platinum wire inserted through the cell base. An alternative cell has also been designed which permits the use of standard reference electrodes.

The polarizable electrode functions most effectively when the periphery of the mercury meniscus is close to or level with the top of the electrode tube; the diffusion currents are then invariant with time, thus conforming with the condition for spherical diffusion. On the other hand if the meniscus is withdrawn to a depth of 2 cm or more below the rim of the electrode tube, it is found that the diffusion currents decrease with time in a hyperbolic manner suggesting that under these conditions the diffusion may be linear in character (Fig. 4).

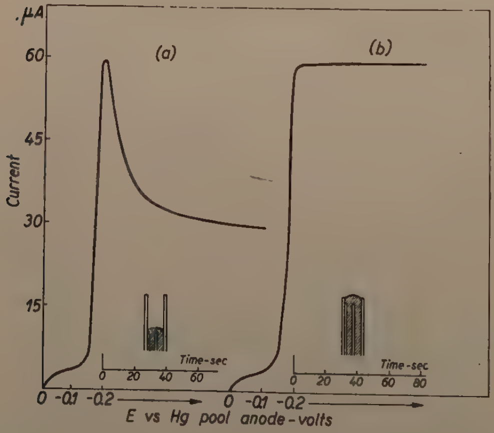

Fig. 4. Influence of meniscus position on the diffusion current for 2.05 m*M* Sb^{+3} in normal hydrochloric acid.
(a) Shielded meniscus. — Linear diffusion curve.
(b) Exposed meniscus. — Spherical diffusion plateau.

The height of the column of mercury in the electrode tube is governed partly by the level of the amalgam in the reservoir and partly by the rate of supply of fresh mercury. The rate of supply of fresh mercury is equal to the rate at which mercury issues from the dropping mercury electrode; this rate is reasonably constant and normally produces a kinetic head at the electrode of $1^1/_2$ mm Hg. Thus mercury height control may be exercised solely by adjustment of the height of the reservoir. In practice accurate control is more conveniently obtained by

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adjustment of the height of the electrode and cell with respect to the reservoir by means of a micrometer screw attached to the cell mounting. The reservoir has a surface area of 236 sq.cm, and affords adequate capacity for amalgam thus effectively preventing any significant change in meniscus level at the electrode. The cell has a remarkably low resistance of the order of tens of ohms.

The top of the feed tube is normally positioned $1^1/_2$ mm below the crown of the meniscus; if the feed tube is withdrawn below this level the diffusion currents develop pronounced maxima. These maxima progressively disappear when the feed tube is gradually restored to its normal position (Fig. 5).

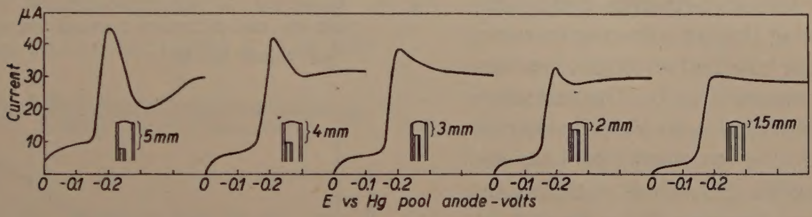

Fig. 5. Influence of position of feed tube on the diffusion current for 2.05 mM Sb^{+3} in normal hydrochloric acid. Diffusion current curves produced with Hg feed tube at varying depth below meniscus.

RESULTS

The polarographic waves obtained with air-free solutions of antimony trioxide in normal hydrochloric acid are found to be reproducible (Fig. 6). The waves are similarly shaped to those obtained with the dropping mercury electrode. Furthermore the continuous character of the mercury feed permits the waves to be recorded as smooth curves without the oscillations which characterise the waves obtained at the dropping mercury electrode. Oxygen interferes and must be removed from the solution by passing oxygen-free nitrogen for 15 minutes.

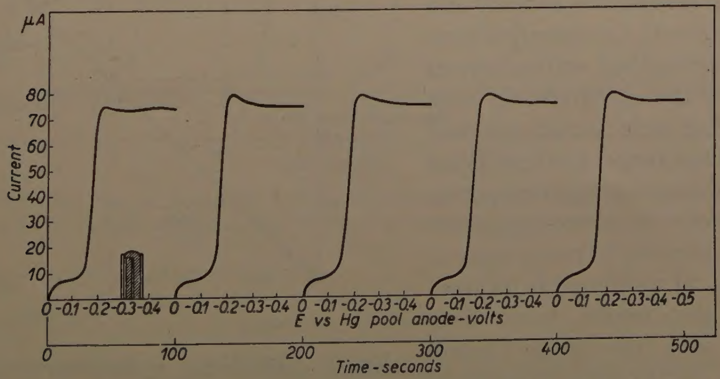

Fig. 6. Reproducibility of diffusion current. Polarograms for 2.2 mM Sb^{+3} in normal hydrochloric acid.

Polarographic waves for solutions of varying antimony concentration[9] are shown in Fig. 7. A plot of the wave height against concentration shows a linear relationship (Fig. 8) indicating that diffusion currents are proportional to the concentration of the trivalent antimony ion. The log plot of the wave yields a straight line having a reciprocal slope of 0.020 volts, the theoretical value for a 3-electron reduction, indicating that at a flowing mercury electrode trivalent antimony is reversibly reduced (Fig. 9). The half wave potential of —0.16 volts measured against the mercury pool anode agrees with the values obtained by other workers for the reduction of trivalent antimony in normal hydrochloric acid using the dropping mercury electrode[10-18].

It might be expected that electro-capillarity at the flowing mercury electrode would manifest itself by a vertical displacement of the mercury meniscus during the application of a varying potential. This aspect has accordingly been investigated with the aid of a travelling microscope, over the applied negative potential range 0 - 2.6 volts against the mercury pool anode with solutions of lead nitrate of 1 mM and 0.5 mM strength. Comparative tests were also carried out with no flow of mercury at the electrode. In each case ten tests were carried out over the full voltage range, five tests being run with increasing negative potential and five with decreasing potential. The variation between tests of a similar kind was found to be insignificant; the results have been averaged and the mean values are shown plotted against potential in Fig 10. At potentials below 0.2 volts

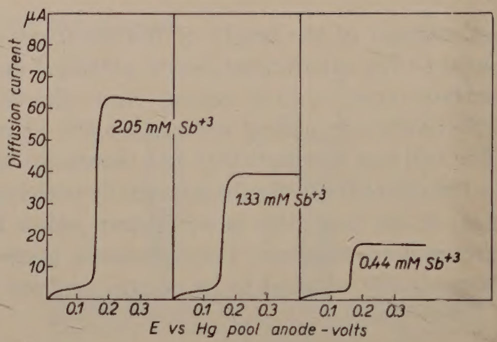

Fig. 7. Influence of concentration of reducible ion on the diffusion current for solutions of Sb_2O_3 in normal hydrochloric acid.

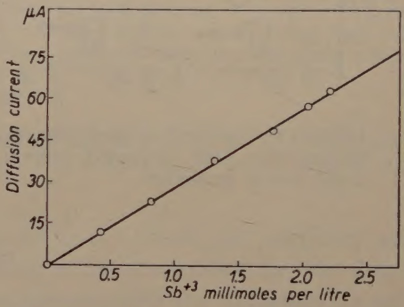

Fig. 8. Concentration-Diffusion current relation ship for the polarographic waves shown in Fig. 7.

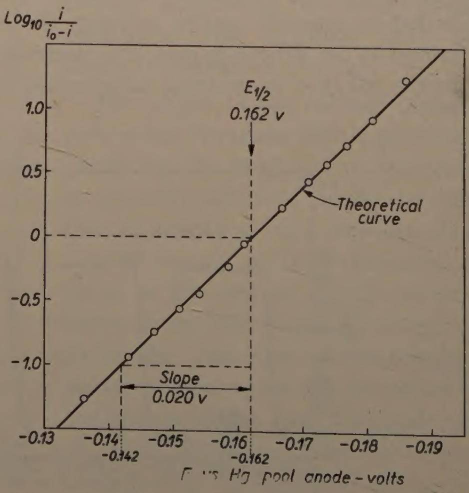

Fig. 9. Plot of log $\frac{i}{i_d - i}$ for the reversible reduction of Sb^{+3} in normal hydrochloric acid at the the flowing mercury electrode.

the displacement of the meniscus is insignificant but at potentials approaching 0.5 volts the vertical displacement approaches 1 mm in magnitude. It will be noted that the shape of the curves reflects the electro-capillary curve for mercury.

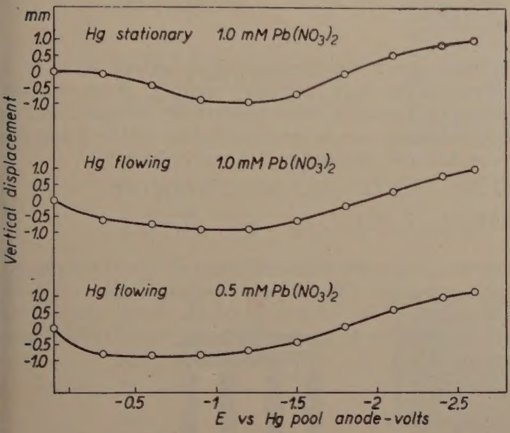

Fig. 10. Influence of electro-capillarity at the flowing mercury electrode.

The effect of repeated polarographic reduction at a stationary mercury surface has also been investigated. The resulting current-voltage curves are shown in Fig. 11. As would be expected these curves have a similar shape to the curve obtained with mercury flowing but with the feed tube withdrawn to a depth of 5 mm below the electrode surface (Fig. 6). It is significant that, after a series of five runs with a static mercury surface, the current maximum increased in magnitude by over 20% but that a change of surface produced a restoration of the maximum current to the initial value once more.

The polarograms recorded in this paper were obtained with a Cambridge Photographic Recording Polarograph. Polarographic studies in fluoride media with the flowing mercury electrode are proceeding and will be reported in Part II.

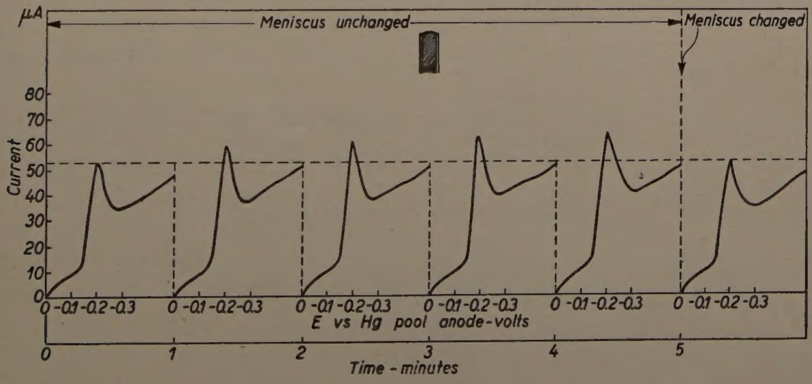

Fig. 11. Polarographic waves obtained with a stationary mercury surface exposed at the electrode tube. — Curves obtained with fresh, stagnating and renewed mercury surfaces.

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SUMMARY

A polarisable electrode of constant surface area is described in which the surface layer of a column of mercury is continuously renewed from an internal mercury supply. Reproducible diffusion currents are obtainable which do not exhibit maxima. Wave heights are proportional to the concentration of reducible ion. The mercury consumption is similar to that of the dropping mercury electrode. The electrode and cell are constructed throughout in polyethylene.

RÉSUMÉ

Une électrode polarisable est décrite, où la surface de mercure de la colonne est continuellement renouvelée. Des courants de diffusion reproductibles peuvent être obtenus, ne présentant pas de maxima. Les hauteurs des sauts sont proportionnelles à la concentration de l'ion réduit. La consommation de mercure est la même que celle de l'électrode à gouttes de mercure. L'électrode et la cuve sont entièrement faites en polyéthylène.

ZUSAMMENFASSUNG

Es wird eine polarisierbare Elektrode beschrieben, wo die Oberfläche des Quecksilbers ständig erneuert wird. Es können reproduzierbare Diffusionsströme erhalten werden, welche keine Maxima aufweisen. Die Höhen der Sprünge sind proportional der Konzentration des reduzierten Ions. Der Verbrauch an Quecksilber ist der gleiche wie der, der Tropfelektrode. Die Elektrode und die Zelle sind ganz aus Polyäthylen hergestellt.

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